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REDUCTION OF ATMOSPHERIC POLLUTION BY THE APPLICATION OF FLUIDIZED-BED COMBUSTION

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by

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ABSTRACT

Combustion of fossil fuels in a fluidized bed consisting of partially reacted limestone is being studied to determine the effect of operating variables on pollutant SO_2 and NO_x emission in the flue gas. Coal has been burned with either an excess or deficiency of oxygen in a 6-in.-dia bench-scale combustor operating at atmospheric pressure with a bed of partially reacted limestone (which is the acceptor for the sulfur compounds released during combustion). The mechanism of sulfur capture has been studied. Preliminary data have been obtained on conditions for regeneration of the sulfur-containing acceptor for recycle to the combustor. A mathematical model has been developed to predict the retention of sulfur at different operating conditions when coal is burned in a fluidized bed.

SUMMARY

The Office of Air Programs of the Environmental Protection Agency is funding an investigation at Argonne National Laboratory of the effects of variables on the removal of atmospheric pollutants (oxides of sulfur and nitrogen) generated during the combustion of fossil fuels in a fluidized bed. The concept involves burning fuel (coal, oil, or natural gas) in a fluidized bed of particulate solids that react with gaseous sulfur compounds (and possibly nitrogen compounds) released during combustion. A fluidized bed is a highly efficient contacting medium for carrying out gas-solid reactions and for removing heat generated by combustion.

The fluidized-bed combustion equipment at Argonne consists of a 6-in.-dia, 6-ft-long bench-scale combustor operated in series with a 3-in.-dia, 7-ft-long gas preheater section. Ancillary equipment for operation of the combustor includes mechanical powder feeders for introducing coal and additive into the combustor, gas manifolding for the air supply to the combustor, cyclone separators and a final filter for removing particulates from the flue gas, and a flue gas sampling and analytical system.

Bench-Scale Combustion Experiments

Experiments have been performed to investigate the effects of operating variables on SO_2 and NO levels in the flue gas. Variables affecting the chemical composition and physical properties of the bed and elutriated particles have been studied, and material balances have been obtained for some experiments. Except in a few runs in which the fluidized bed was alumina or coal ash particles, the fluidized bed consisted of partially reacted limestone, which reacts with the sulfur compounds. The combustor was operated in the single-stage and two-stage modes.

In single- or one-stage combustion, more than the stoichiometric quantity of oxygen (as air) is added to the fluidized-bed combustion zone to burn the coal to CO_2 and water. Typically, the flue gas coming from the bed contains ∿3% oxygen. In two-stage combustion, less than the stoichiometric volume of air is added to the first stage. The oxygen concentration of the gas leaving this stage is approximately zero or near zero and, because relatively large amounts of CO and hydrocarbons are produced, the atmosphere is highly reducing. As a process concept, the CO and hydrocarbons from this stage could be burned in a second stage. The second stage could be physically separate from the first stage but in the ANL combustor consists of the freeboard volume above the fluidized bed. Enough air is injected into the second stage so that in most runs the oxygen concentration in the flue gas is ∿3%.

Major findings in the one-stage combustion experiments were that retention of sulfur in the bed is strongly influenced by the following operating variables over the range of the operating variables tested:

1. Fluidized-bed temperature. Maximum sulfur retention was noted at different temperatures (e.g., 1450 and 1550°F) for different feed materials and operating conditions.
2. Ca/S mole ratio (ratio of moles of calcium in the additive to moles of sulfur in the coal). Sulfur retention increases rapidly as the Ca/S ratio is increased to 3 and then increases less rapidly as the Ca/S ratio is further increased.
3. Superficial gas velocity. Sulfur retention decreases as the gas velocity is increased. At a Ca/S ratio of ∿4, sulfur retention decreases approximately 5% for each 1 ft/sec increase in gas velocity in the range 2.0 to 7.6 ft/sec. At lower Ca/S ratios, the decrease in sulfur retention is greater than 5% per ft/sec increase in gas velocity; at higher ratios, sulfur retention may be essentially independent of gas velocity.

Variables that have a lesser effect on sulfur retention over the ranges studied include the following:

1. type of coal
2. coal particle size
3. limestone type
4. limestone particle size
5. fluidized-bed height
6. excess combustion air
7. moisture
8. solids feeding method
9. temperature of the upper stage of the combustor

The effects of several operating variables on NO level in the flue gas were also observed. When water was injected in the base of the bed at rates representing a range of moisture contents of different coals, the NO concentration in the flue gas decreased from 530 ppm with no water addition to 380 ppm with water added at a rate corresponding to a coal moisture content of 51%. It was also observed that NO concentration, normally 300-600 ppm in one-stage runs, is reduced to less than 80 ppm (only a little above the equilibrium level expected from the nitrogen-oxygen reaction) in two-stage combustion runs.

Further details are given below for the experiments that provide the basis for these observations.

Fluidized-Bed Temperature. In runs with Pittsburgh seam coal and limestone No. 1359 at a Ca/S ratio of ~4.2 and with a gas velocity of ~2.6 ft/sec, sulfur retention (as a percentage of the sulfur in the feed streams) increased from 78% to 96-99% as the fluidized-bed temperature was increased from 1325 to 1450°F, and then decreased to 60% as the temperature was further increased to 1650°F. Thus, ~1450°F was the optimum temperature for reducing SO_2 emissions when using this coal under the above operating conditions. In contrast, an optimum temperature of 1550°F was observed in earlier work with Illinois coal, a different batch of No. 1359 limestone, a lower Ca/S ratio of 2.5, and a gas velocity of ~3 ft/sec (ANL/ES/CEN-1002, p. 35).

Ca/S Mole Ratio. The effect on sulfur retention of Ca/S mole ratio was studied in two series of runs using different coals and different additive particle sizes. Using Pittsburgh coal and -14 mesh limestone No. 1359 at a fluidized-bed temperature of 1450°F, sulfur retention increased from 46% at a Ca/S ratio of ~1.0 to 96-99% at a Ca/S ratio of 4.2. With Illinois coal and -14 mesh limestone No. 1359 at a temperature of 1550°F, the sulfur retentions were 78, 95, and 94%, respectively, at Ca/S stoichiometric ratios of 2.5, 4.6, and 5.5.

Data on the effect of Ca/S mole ratio was obtained also in runs with two 6-in.-dia combustors, one at Argonne National Laboratory and the other at the National Coal Board's Coal Research Establishment Laboratories (CRE) in England. In these experiments, Ca/S mole ratios of 1-3 were used at a bed temperature of 1472°F. Various combinations of American and British materials (British Welbeck coal, American No. 1359 limestone, Illinois coal, and British Stoke-on-Kent limestone) were tested at both installations. The SO_2 levels in the flue gas for ANL runs agreed reasonably well with those of CRE and showed again that increasing the Ca/S ratio increased the sulfur retention.

Type of Coal. Data from experiments using limestone No. 1359 at fluidized-bed temperatures of 1450-1470°F and Ca/S ratios of 1 to 4.3 indicated little difference in results when using either Illinois coal or Pittsburgh coal at sulfur retentions of less than 90%. Additional data would be required at other temperatures before a complete analysis can be made.

Coal Particle Size. In experiments with -12 +50 mesh and -50 mesh Illinois coal (a -12 +50 mesh fraction ground to -50 mesh), a Ca/S mole feed ratio of 2.4, and a fluidized-bed temperature of 1550°F, the sulfur retention was 81% and 75% for the two size fractions. These sulfur retentions were compared with a sulfur retention of 78% obtained in an experiment performed with -14 mesh coal at nearly identical operating conditions. The results indicate a slight benefit from burning coarse coals or coal containing small amounts of small particles.

Type of Additive. Sulfur retentions for several types of additive were compared in runs performed at a Ca/S mole ratio of 2.5. With limestone No. 1359 at 1550°F, sulfur retention was 78%, which is comparable to that obtained with limestone No. 1360 and dolomite No. 1337 at combustion temperatures of 1550-1600°F. This indicates that differences in these additive types had minimal effects at the temperatures studied.

In runs with American and British coal-limestone combinations, the reactivity of the British and American limestones was compared. Results showed that the particular type of British limestone used removed a greater fraction of the SO_2 from the combustion gases than did the American limestone, but the effect was not large.

Additive Particle Size. Limestone No. 1359 of 1000-μm average particle diameter and limestones No. 1359 and 1360 and dolomite No. 1337 of 490- to 630-μm particle size were compared at a Ca/S mole ratio of 4.0 and a superficial gas velocity of 3.0 ft/sec. (Some sulfur retention values were calculated by extrapolation or interpolation of experimental values.) Sulfur retention was ∿87% for the larger-particle additive and 93% for the smaller-particle additives, indicating that additive particle size, within the range tested, has only a moderate effect on sulfur retention at a particular fluidizing-gas velocity.

Fluidized-Bed Height. To determine the effect of fluidized-bed height on sulfur retention, three one-stage combustion runs were made under similar conditions but with fluidized-bed heights of 14, 24, and 46 in. Sulfur retentions were 80, 81, and 85%, respectively, indicating only a minor effect of bed height.

Superficial Gas Velocity. The effect of superficial gas velocity in the combustor on sulfur retention was examined in several series of runs. As an illustration, in one series of combustion experiments with Illinois coal, coarse particles of limestone No. 1359 with diameters averaging 1010 μm were fed to the fluid bed to ensure their retention in the bed at the highest gas velocity tested. The tests were made at 1550°F with a Ca/S mole ratio in the feed of ∿4 and at gas velocities of 3.5, 5.5, and 7.4 ft/sec. Sulfur retentions were 83, 71, and 63%, illustrating an important effect of gas velocity.

Excess Combustion Air. The effect on sulfur retention of oxygen concentration in the flue gas (controlled by varying the volume of excess oxygen in the feed) was investigated for oxygen concentrations in the flue gas of ∿1 to ∿5 vol % (5.5-32% excess air). An experiment was performed at 1550°F, using limestone No. 1359 additive, Illinois coal, and a Ca/S mole ratio of ∿2.8. In this experiment, sulfur retention was 67% with 0.7 vol % oxygen in the flue gas, 71% with 2.4 vol % oxygen in the flue gas, and 75% with

5.6 vol % oxygen in the flue gas, showing a slight enhancement in sulfur retention at higher excess air.

Moisture Content of Coal. The effect of moisture content of the coal was examined by injecting water at different rates into the base of the fluidized bed during combustion of Pittsburgh coal with limestone No. 1359 additive. (Pittsburgh coal contains 1.8% water and Illinois coal 10.1% water.) The fluidized-bed temperature was 1450°F and the Ca/S ratio was 1. Sulfur retention was not significantly influenced by moisture additions equivalent to burning coal with moisture contents up to 51 wt %; the concentrations of NO, CH_4, and CO in the flue gas decreased when moisture was added.

Solids Feeding Method. The difference in solids feeding methods for the British and American combustors was considered a possible reason for SO_2 levels in the flue gas being slightly higher (by 100-200 ppm) in tests at ANL than in tests at the Coal Research Establishment (CRE) with identical coal and limestone. Premixed coal and limestone were fed through a single line into the British combustor; coal and limestone were fed through separate lines into the ANL combustor. When a mixture of American coal and limestone was fed into the ANL combustor, sulfur retention did not differ significantly from that obtained when coal and limestone were fed separately, indicating that slight differences in ANL and CRE data cannot be attributed to the feeding method.

Temperature of the Freeboard. Tests were performed to determine if any appreciable fraction of SO_2 reaction with additive was occurring in the gas space above the fluidized bed. In one experiment, the upper section of the ANL combustor (above the fluidized-bed combustion zone) was insulated, thereby increasing the temperature in that zone to 1340°F as compared with 1020°F in the absence of insulation; the temperature of the fluidized bed was 1450°F. Insulation of the upper section had essentially no effect on sulfur retention but resulted in lower concentrations of CH_4 and NO in the flue gas. These results suggest that sulfur-removal reactions occurred essentially in the fluidized-bed zone, but that combustion of CH_4 and decomposition of NO increased when the upper combustor section was at 1340°F. Insulation of the upper section of the combustor also slightly increased the amount of CO burned.

Absence of Additive. Experiments were performed to determine how much of the sulfur in coal is actually released as SO_2 during combustion, since some sulfur can be retained by ash constituents. Illinois and Pittsburgh coals were burned in a fluidized bed of refractory alumina with no additive present and at a nearly constant coal feed rate (about 4 lb/hr). With fluidized-bed temperatures ranging from 1325 to 1650°F, the concentrations of SO_2 in the flue gas were 1900 to 2200 ppm when Pittsburgh coal (2.4 wt % S) was burned and 3750 to 4250 ppm when Illinois coal (3.7 wt % S) was burned. The observed SO_2 levels when Pittsburgh coal was burned were 150-300 ppm less than the levels calculated for complete release of all sulfur as SO_2. For Illinois coal, the observed SO_2 levels and the calculated levels for complete release of sulfur as SO_2 were approximately the same.

NO Content of Flue Gas. To determine the effect of additive on NO content of the flue gas, five experiments were performed with Pittsburgh coal at temperatures of 1325-1650°F, with no additive present, a coal feed rate of 4 lb/hr, and fluidizing gas velocities of 2.4 to 2.8 ft/sec. NO concentrations in the flue gas ranged from 450 to 630 ppm.

In experiments with Illinois coal, limestone No. 1359 additive, a fluidized-bed temperature of 1550°F, a Ca/S mole ratio of ∿4, and superficial gas velocities of 3.5 to 7.4 ft/sec, nitric oxide concentration in the flue gas ranged from 320 to 470 ppm. This is an indicated reduction in NO emission of 20 to 45% as compared with NO emission in the absence of additive.

The effect of moisture content of the coal on NO level in the flue gas was studied by adding water to the fluidizing air at different rates during the combustion of Pittsburgh coal. Limestone No. 1359 additive was used at 1450°F and a Ca/S ratio of 1. The concentration of NO decreased from 530 ppm to 510 ppm upon adding 10 cc/min water (equivalent to 26 wt % water in the coal) and to 380 ppm when the rate of water addition was increased to 30 cc/min (equivalent to 51 wt % water in the coal).

Chemical Composition and Physical Properties of Bed and Elutriated Materials. To determine the extent of calcination (to CaO) of bed and elutriated materials, samples from several series of bench-scale experiments were analyzed for calcium, sulfur, and carbonate contents. Calcination of the limestone in the fluidized-bed and final-filter solids was essentially complete (95% or greater); for solids in the cyclones, calcination ranged from 60 to 84%.

The extent of calcium utilization (i.e., conversion of CaO to $CaSO_4$) in the bed and elutriated materials from several series of runs was determined from analytical results. A higher degree of calcium utilization in the fluid-bed solids was observed in a series of runs utilizing a small-particle-size additive (25-103 μm) than in runs using larger particle size additive (average particle sizes of 44-650 μm; 490 μm; 1640 μm). The Ca/S mole ratios in fluidized-bed and final-filter solids (0.9-3.4) were near the Ca/S mole ratios of the input coal and limestone streams (1-3.6). The Ca/S mole ratio for cyclone solids was as high as 11, indicating a low degree of sulfation of this material (probably due to a shorter residence time in the combustor reaction zone).

To measure any changes in particle size distributions during the runs, particle-size analyses were performed on fluidized-bed solids from several experiments. Results showed that particle size distributions of bed samples taken during a run were related to the size distribution of the initial bed material and were similar to the size distribution of that fraction of the fresh additive that was not capable of being elutriated at the gas velocity existing in the combustor.

The decrepitation and attrition of several additives during coal combustion has been estimated by comparing the quantity of small-particle additive fed in a run to the quantity of additive elutriated. Results indicated that the decrepitation rates of limestone No. 1359 and British limestone are low. Limestones of this type are, therefore, desirable materials for use in a full-scale fluidized-bed combustor with regeneration and recycle of additive. High carryover of additive was observed when limestone No. 1360 and dolomite No. 1337 were used, indicating that these may be less promising materials for regeneration and recycle.

The bulk and tapped densities of samples of solids from the fluidized bed, cyclones, and final filter were determined. Bulk densities of the cyclone and final-filter solids were low, 0.15-0.77 g/cc, probably because of the nature of the solids, which consisted of flyash and/or limestone fines. The bulk and tapped densities of the fluidized-bed solids were very similar to those of the precursor solids (limestone and coal ash).

Sulfur, carbon, and calcium material balances have been completed for a large number of runs. Material balances ranged from 83 to 114%.

Two-Stage Combustion Experiments. In two-stage combustion, a substoichiometric volume of combustion air is fed at the base of the fluidized bed, and a second volume of air is added at a point 6 in. above the bed to burn CO and hydrocarbons in the gas leaving the fluidized bed. In the first two exploratory runs, the secondary air was injected downward (toward the bed and countercurrently to the fluidizing-gas flow); in two other exploratory runs, air was injected upward (away from the bed and cocurrently with the fluidizing-gas flow). These runs were made with Illinois coal and limestone No. 1359 additive. The Ca/S mole ratio was ∿3, and the fluidizing-gas velocity was ∿1.9 ft/sec. The starting bed was partially sulfated and calcined limestone No. 1359.

The results for the two-stage runs with upward flow of secondary air showed a maximum SO_2 removal of 91% at a Ca/S ratio of 3.0. The NO level in the flue gas was 70 ppm, the lowest value recorded at ANL thus far. Downward flow of secondary air resulted in poor SO_2 removals. Possibly, the downward-directed air contacted the bed solids releasing SO_2 by reaction with calcium sulfide. Sulfide has been qualitatively identified in bed samples from these runs.

Mechanism of Lime Sulfation Reaction

Studies have been made on the lime-SO_2 reaction mechanism, specifically on the mode of SO_2 penetration into lime particles in fluidized beds. In this laboratory, it is believed that the mechanism is essentially the shell-formation model enhanced by localized reducing conditions in the dense phase* of the fluid bed. Because of a large demand for oxygen by the carbon combustion reaction near the bottom of the combustor, the emulsion phase in this location is depleted in oxygen relative to the bubble phase. As a result, the CO concentration is relatively high at some locations in the dense phase where the SO_2-lime reaction takes place.

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*The dense or emulsion phase is the portion of the bed where gas flows in intimate contact with the solids. The remainder of the gas passes through the bed in the form of bubbles, but as the bubbles rise through the bed, gas circulates from the bubbles into the emulsion phase and back into the bubbles. The gas in the bubble phase is available for reaction only as rapidly as it circulates into the emulsion phase.

ANL work reported here on the mechanism comprises (1) electron microprobe examination of sulfated lime particles taken from elutriated solids and from combustor beds and (2) laboratory-scale experiments with sulfated lime to measure SO_2 evolution under reducing conditions. Microprobe examination of particles taken from the combustor bed during coal-combustion experiments showed that some particles had nearly uniform sulfur distributions across the particle diameter and other particles had deep sulfur penetration (but not all the way to the center).

Microprobe examination of particles taken during an experiment in which calcined limestone was exposed to an SO_2-air mixture (with no combustion occurring) showed that this sulfur profile was radically different from the sulfur profile of particles from a coal combustion experiment in which all operating conditions other than the presence of combustion were similar. Sulfur formed a very thin shell on the surface of the particles from the former experiment. Furthermore, the thickness of this layer did not change appreciably with increasing reaction time and was considerably thinner than in lime particles from the coal combustion experiment. The conclusion from these microprobe examinations is that sulfation reactions during the combustion of carbon differ from sulfation reactions in the absence of combustion. Although it cannot be said that the mechanisms of the reactions are different, the extent of the sulfation reaction is considerably greater for the combustion case. This lends support to the hypothesis that local reducing conditions existing during combustion produce mobility of the SO_2 for penetration into the lime particles.

Laboratory-scale experiments to determine the effect of CO on the sulfation reaction showed that SO_2 can be released readily from sulfated lime at about 1750°F, using CO as the reductant. At lower temperatures (∿1650°F), the reduction reaction apparently produces CaS rather than CaO and SO_2 since SO_2 is released in high concentrations when air is passed through a bed of sulfated lime that has been treated with CO at the lower temperature. In experiments in which the temperature of the reaction was 1500°F, the rate of reaction to form CaS was nearly zero.

Regeneration of CaO from $CaSO_4$

Since efficient SO_2 removal from the gas phase in coal combustion will probably require relatively large quantities of limestone, it will be desirable to regenerate the partially sulfated lime for recycle and to recover the sulfur value as sulfuric acid or elemental sulfur. Thermodynamic equilibria for the regeneration of sulfated lime using CO have been analyzed.

Operation at 10-atm pressure is being considered for both fluidized-bed combustion and regeneration. The equilibrium values for the reaction of $CaSO_4$ with carbon monoxide, derived from free energy data, were used to calculate the SO_2 partial pressure at 1- and 10-atm system pressures over the temperature range 1400-2000°F. The SO_2 generation reactions are pressure dependent, and increasing the system pressure reduces the SO_2 concentration proportionately.

Laboratory-scale experimental work has been started to examine the utility of various regeneration reaction schemes. Two preliminary batch fluidized-bed experiments (in a 2-in.-dia reactor) were performed at 1950°F with a superficial gas velocity of 2 ft/sec and an inlet gas stream containing 10 vol % CO, 20 vol % CO_2, and nitrogen (with oxygen added to burn CO and maintain the desired combustor temperature). One experiment was performed at a pressure of 1 atm and the second experiment at 10 atm.

At 1-atm pressure, the maximum SO_2 concentration in the effluent gas phase was about 3 vol %. Equilibrium calculations predicted a concentration value of about 8 vol %. About 80% of the sulfur contained in the original sample of partially sulfated limestone was evolved as SO_2. Of the sulfur remaining in the particulate residue, about 90% was present as the sulfide, CaS.

In the experiment performed at a total pressure of 10 atm, it proved difficult to maintain a constant temperature, and a temperature excursion resulted in partial caking of the bed material. The little SO_2 evolved during this experiment was released mainly during the heatup period.

Modelling Studies, SO_2 Removal

A mathematical model was devised for predicting, from the fluidized-bed reaction parameters, sulfur retention in a fluidized bed by heterogeneous reaction with additive limestone particles. The model was fitted to experimental data and gave reasonably good agreement with observed sulfur retention.

Control of Chloride Emission

To examine the potential of fluidized-bed combustion for the control of chloride emission, thermodynamic equilibria were examined for several reactions in which hydrogen chloride is reacted with solids. Hydrogen chloride is produced (1) during combustion of coal (since most coals in the United States contain chlorides) and (2) during the incineration of chloride-bearing wastes such as polyvinyl chloride plastics. At a combustion temperature of 1500°F and with 10 vol % water present, reaction of HCl with lime does not reduce the hydrogen chloride concentration in the flue gas below 1000 ppm. At these conditions, BaO, KOH, and NaOH remove HCl more effectively than does lime, and MgO is less effective than lime. Small amounts of BaO, KOH, or NaOH along with limestone possibly would remove HCl from the gas phase.

I. INTRODUCTION

Methods are being developed for lowering the concentrations of noxious pollutants emitted from power- and steam-producing plants to meet standards set by state and federal governmental agencies. Progress is reported here on a continuing study of the removal of pollutant (SO_2, NO, particulate) from the gas phase in the combustion of fossil fuels (such as coal, oil, and natural gas). The concept investigated involves introducing fuel and a sulfur-reactant additive material such as crushed limestone into a hot fluidized bed of solids. Sulfur dioxide is generated when sulfur-containing fuel burns in an excess oxygen atmosphere and reacts with calcined limestone, forming solid $CaSO_4$ particles.

During the first two years of this investigation, the effects of independent variables on the reduction of SO_2 and NO levels in the flue gas have been studied at this site with a 6-in.-dia bench-scale combustor operated at atmospheric pressure. A fine (<44 mesh) limestone additive was generally used, and these data were supplemented by SO_2-additive reaction rate data obtained in boat reactor experiments. Coal was the fuel burned in most tests, but in a few, natural gas was combusted to demonstrate the low NO levels achievable and to show that a source of the NO formed during coal combustion is nitrogenous compounds in the coal. The combustor was operated as a one-stage unit in this earlier work; in one-stage combustion, all of the combustion air is added to the fluidized-bed region, where essentially all combustion takes place in the presence of excess oxygen.

The ANL work reported here consisted of three major parts-- (1) bench-scale experiments to study the effects of variables and combustion mode on sulfur retention in the fluidized bed, NO removal, and bed particle composition and size; (2) laboratory-scale investigations of the mechanism of lime sulfation, and (3) the development of models to allow the extent of sulfur retention to be predicted from the fluidized-bed reaction parameters.

Work at the Chemical Engineering Division of ANL during the past three years has complemented studies of other contractors of the Environmental Protection Agency's Office of Air Programs (OAP)--British National Coal Board; Esso Research Center, Ltd.; Esso Research and Engineering; Pope, Evans, and Robbins; Consolidation Coal; U.S. Bureau of Mines; and Westinghouse. The program developed by OAP should result in lower pollutant concentrations in the air and secondarily may result in a more economical combustion process.

The objectives of the development program at ANL are:

1. To determine how sulfur retention and limestone utilization are affected by independent fluidized-bed operating variables, such as bed temperature, combustor pressure, gas velocity, oxygen concentration, bed height, calcium-to-sulfur ratio, type of additive and coal, and additive and coal particle size.

2. To determine the effect of operating variables on the level of NO in the flue gas.

3. To compare, as a function of the independent operating variables, the characteristics and quantities of flyash generated in fluidized-bed combustors and in conventional pulverized-fuel boilers.

4. To determine the effects of independent operating variables on the regeneration of sulfated additive material and to investigate various methods of regenerating this additive at elevated pressures.

5. To determine how effectively the regenerated additive removes SO_2 from the flue gas.

6. To determine the chemical and physical mechanisms involved in
    a. removal of SO_2 by additive
    b. NO formation
    c. regeneration of additive

II. BENCH-SCALE COMBUSTION EXPERIMENTS

The bench-scale combustor has been operated in the single-stage and two-stage modes in experiments to investigate the effects of operating variables on sulfur retention in the fluidized bed and NO removal from the flue gas. Variables affecting the chemical composition and physical properties of bed and elutriated particles have been studied, and material balances have been obtained for some experiments.

Additional data have been obtained for the BC- and AR-series of experiments discussed in the preceding annual report (ANL/ES/CEN-1002). New experiments performed were the Amer, Brit, Hump, HP, and PBY series.

A. Materials

1. Coal

The coals used in the various series of experiments were Illinois coal from Seam 6, Peabody Coal Co. Mine 10, Christian County, Illinois (furnished by Commonwealth Edison); Pittsburgh Seam coal from Humphrey Preparation Plant, Osage, West Virginia; and Welbeck coal (furnished by the British National Coal Board).

The Illinois coal used in the experiments contained 3.77 wt % sulfur and generally was crushed to pass a -14 mesh sieve. The sieve analysis of this coal is given in Table A.1 of Appendix A of this report, and its chemical characteristics in Table A.2. For experiments PB-5R and -6R, coal from this batch was crushed and screened; the -12 +50 mesh fraction was divided into two portions. One portion was fed in experiment PB-5R. The remaining portion was crushed and screened again to obtain a -50 mesh fraction, which was fed in experiment PB-6R. The size distribution of the Illinois coal used in experiment AR-6 is given in Table A.3.

Size distributions and chemical characteristics of the Welbeck coal (containing 1.2 wt % sulfur) are given in Tables A.1 and A.2. The proximate analysis, ultimate analysis, and particle size distribution of the Pittsburgh coal which contained 2.4 wt % sulfur are given in Table A.4.

2. Additives

Limestone No. 1359, used in many experiments performed during the report period, was obtained from M. J. Grove Lime Co., Stephens City, Va. and contained 95 wt % $CaCO_3$ and 1 wt % $MgCO_3$. The particle size distributions of limestone No. 1359 before and after passage through the screw feeder are given in Table A.3. Attrition of the limestone during passage through the volumetric screw feeder resulted in the average particle diameter decreasing from 1637 μm to approximately 1000 μm. The limestone used in experiment AR-6 is that identified as "Limestone after Passage through Screw Feeder."

The chemical compositions and size distributions of the limestones used in the Amer-Brit series experiments are given in Tables A.5 and A.6. That supplied by the British National Coal Board (J. Gregory & Son, Stoke-on-Kent, Staffordshire) contained, on an as-received basis, 95.6% $CaCO_3$ (average of two analyses).

3. Bed Material

In most of the bench-scale experiments performed during the report period, the starting bed was partially calcined and sulfated limestone from the preceding experiment. Some experiments utilized limestone No. 1359 as the starting bed.

In the experiments employing British coal and limestone, the starting bed material was ash from Welbeck coal. A chemical analysis and a sieve analysis of this ash are listed in Table A.7. Comparison of the chemical analysis for the ash (Table A.7) with that given for the mineral content of Welbeck coal ash (Table A.2) shows reasonable agreement.

In experiments in which coal was burned with no additive present, the starting bed consisted of fused alumina (Type T-61, 30-mesh, manufactured by Alcoa).

B. Bench-Scale Equipment

The fluidized-bed combustion equipment consists of a vertical 6-in.-dia, 6-ft-long fluid-bed combustor, a 3-in.-dia, 7-ft-long preheater for the fluidizing-combustion air (Appendix B, Section 3), vibratory screw feeders for introducing particulate coal and additive into transport air streams that carry these solids to the combustor, gas manifolding for the air supply to the combustor, associated heating and cooling arrangements and controls, the fluidizing-combustion air supply (Appendix B, Section 4), temperature and pressure sensing and display devices, solids and gas sampling arrangements, a data logger (Appendix B, Section 7), and two cyclone separators and a glass fiber final filter for solids removal from the flue gas. A sample stream of flue gas is routed to a gas analysis system (Appendix B, Section 6). The gas analysis section provides in-line measurement of the flue gas components SO_2, NO, CH_4, CO, and O_2 on a continuous basis and of CO_2 on an intermittent basis.

Figure 1 shows the components of the combustion system. The ANL fluidized-bed combustor is described in detail below, and auxiliary equipment in Appendix B. The gas analysis system is described in ANL/ES/CEN-1002, pp. 21-22.

The 6-in.-dia combustor is 6 ft in length and consists of three sections. The middle section (where combustion occurs) is 4 ft long, the top section is 2 ft long, and the bottom section (which contains the gas distribution plate) about 8 in. long. The combustor was constructed principally of type 304 stainless steel.

The 4-ft middle section is fitted with a flange at each end for connection to the lower and upper sections. Four annular chambers 2 1/2 in. high and 8 in. in diameter are spaced 3 1/2 in. apart on the outer surface of the middle section, with the bottom chamber 3 1/2 in. above the bottom flange. These chambers are welded to the combustor section. Air or an air-water mixture is circulated through these annular chambers, permitting heat removal from specific zones of the reactor. Resistance heaters installed between the annular chambers assist in preheating the fluid bed at the start of an experiment and in maintaining the desired temperature during combustion. The heating-cooling system is described in detail in Appendix B, Section 1. At intervals along the length of the combustor, access is provided to its interior for thermocouples, a solids sampling probe, pressure taps. and solids injection probes. Solids injection and removal are discussed in Appendix B, Section 2.

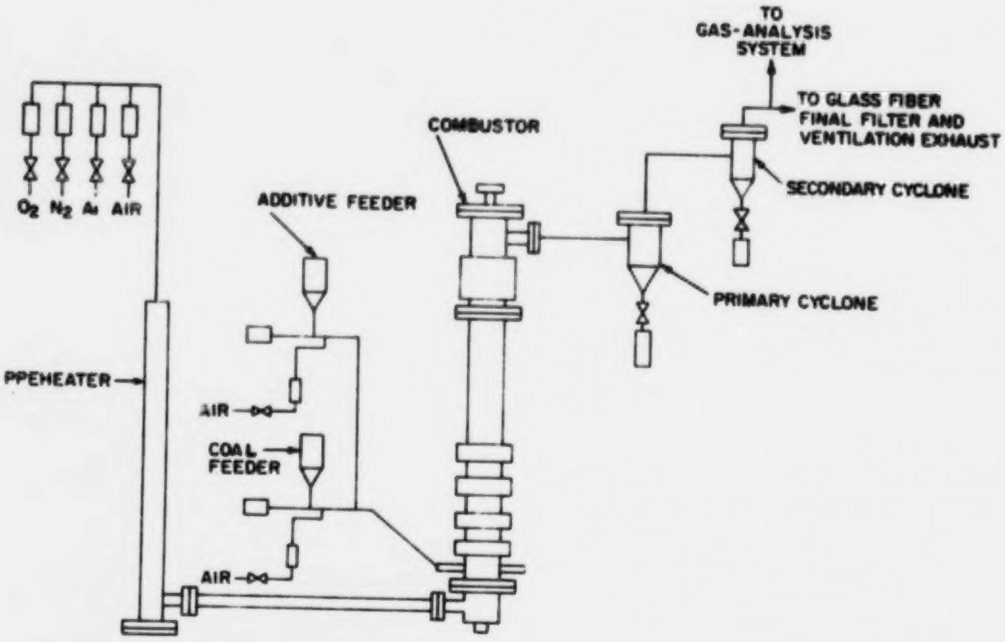

Fig. 1. Simplified Equipment Flowsheet of Bench-Scale Fluidized-Bed Combustor and Associated Equipment

The upper 2-ft-long section is flanged at each end; the upper flange closure contains a sight glass mount. Surrounding most of this section is an annular chamber 12 3/4 in. long and 8 3/8 in. in diameter through which air or air-water mist can be circulated for temperature control. Heat transfer from the gas inside the combustor to the metal wall is facilitated by four fins (1 3/4 in. by 16 in. by 1/16 in.) welded to the interior surface. From the upper section of the combustor, the particle-laden flue gas flows to the cyclone separators and the glass fiber final filter for solids removal. The flue gas filtration system is described in detail in Appendix B, Section 5.

The third section (Fig. 2) of the 6-in.-dia combustor contains the gas distributor and is flanged for connection to the bottom of the 4-ft middle section. On this blind flange are mounted up to 15 bubble-cap type gas distributors, each with eight 1/16-in.-dia holes. The bubble caps are removable so that pressure drop across the gas distributor may be varied if desired. The preheated fluidizing-combustion air enters the plenum below the bubble-cap flange through a pipe at the left in Fig. 2. The welded pipe nipple opposite the flanged pipe furnishes entry for a thermocouple and a pressure tap. A 1 1/2-in. pipe used for withdrawing bed material from the reactor passes through the bottom plate of the plenum and its top is at the face of the bubble-cap plate.

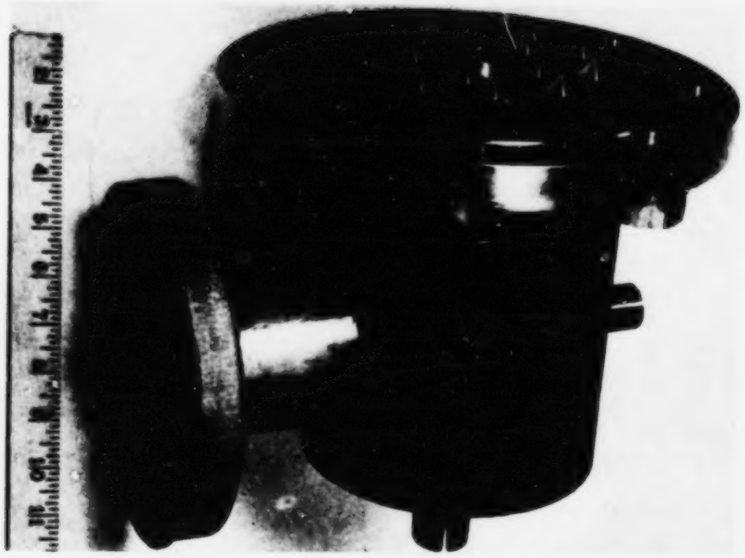

Fig. 2. Bottom Section of ANL 6-in.-dia Fluidized-Bed Combustor

An air feed tube was incorporated into this combustor during some experiments in which the two-stage combustion technique was explored. In two-stage combustion, a deficiency of air is added to the fluid bed through the gas distributor; enough air to complete combustion (i.e., secondary air) is added in the region above the fluidized bed. Feeding of the secondary air was through a 0.25-in.-ID tube installed through the top flange of the combustor so that the tip of the tube was concentrically located 6 in. above the top surface of the fluidized bed. (A 0.25-in.-ID tube was the largest that could be installed without major modification of the combustor.)

C. Procedure

The startup procedure for one-stage coal combustion experiments at ANL involves heating the fluidized bed in the bench-scale combustor to about 800°F by passing air preheated to ~900°F through the bed and simultaneously employing resistance heaters located on the outer surface of the combustor. When the bed temperature reaches 800°F, coal entrained in a transport air stream is injected into the limestone bed and ignites. The burning coal rapidly increases the bed temperature (within one-half hour) to the selected experimental temperature. The selected combustion temperature is maintained within 10°F of the set point (i.e., heat generation is balanced with heat loss from the system) by heating with the external resistance heaters or cooling with air passed through the annular chambers surrounding the middle section of the combustor.

Injection of limestone additive is initiated soon after coal is introduced. The limestone, as is the coal, is carried to the combustor entrained in a transport air stream. Limestone is injected at a feed rate to give the specified Ca/S mole ratio in the feed streams.

To keep the fluidized bed at the specified height, material is removed from the bed, generally once per hour. The quantity of material removed from the bed depends on (1) the quantities of limestone and coal fed and

(2) the quantities of solids elutriated as flyash and removed as bed samples.

As is stated above, the concentrations of O_2, SO_2, NO, CO, and CH_4 in the flue gas are monitored and recorded continuously, and CO_2 concentration is determined periodically. Attainment of steady-state conditions for SO_2 removal from the flue gas is indicated by a relatively steady SO_2 concentration.

At intervals during a steady-state SO_2 removal period and at the end of an experiment, the fluid bed is sampled and at the same time, the elutriated solids collected in the primary and secondary cyclones are sampled. The number of times the bed and cyclone solids are sampled depends on the duration of an experiment.

The solids samples are generally analyzed for C, Ca, S, and $CO_3^=$. Material balances are made based on these analyses to determine carbon burnup efficiency, degree of limestone calcination, limestone utilization, and SO_2 removal.

In two-stage combustion experiments (results are discussed in Section II.D.5), startup is similar to startup in one-stage combustion experiments. Initially, all air is fed at the base of the fluid bed, then the coal feed rate is increased until the oxygen concentration in the flue gas is approximately 2%. The flow rate of primary air fed at the base of the fluid bed is reduced until the oxygen concentration in the flue gas reaches zero, then reduced an additional amount so that a substoichiometric volume of air is being fed to the fluid bed. Flow of secondary air through a tube whose tip is in the freeboard space above the bed is then started, and the oxygen concentration in the flue gas is increased to the desired value.

D. Results and Discussion

The effects of operating variables on sulfur retention in the bed and NO removal during one-stage and two-stage combustion have been studied in experiments using the bench-scale combustor. The effects of variables on the chemical composition and physical properties of bed and elutriated materials have also been investigated. Material balances have been made for several experiments.

Results of Argonne combustion runs are reported as "sulfur retained." That is, the sulfur contained in the SO_2 in the flue gas (measured instrumentally) is compared with the quantity of SO_2 that would be generated from all of the sulfur in the coal fed. Some of the sulfur remains in solid form during a run (e.g., the sulfur contained in fine coal particles that are elutriated out of the bed), and this sulfur content is included in "sulfur retained" values.

1. Effects of Variables on Reduction in SO_2 Emissions during One-Stage Combustion

The variables investigated have been fluidized-bed temperature, Ca/S mole ratio in the feed, combustor design, type and particle size of coal and additive, fluidized-bed height, superficial gas velocity, excess air, moisture content of coal, solids feeding method, temperature of the gas in the freeboard above the fluidized bed, and absence of additive.

Operating conditions and results for most of the experiments completed during the past year have been tabulated as a computer readout and are presented as Table 1.

a. Fluidized-Bed Temperature. Five runs (Hump-1A to -1E) were performed with Pittsburgh coal and limestone No. 1359 (609-μm) to study the effect of fluidized-bed temperature on the percentage of sulfur retained. The temperature of the fluidized bed was varied between ∿1325 and 1650°F, the gas velocity was 2.5-2.9 ft/sec, and the Ca/S ratio was ∿4.2. The data on sulfur retention (as a percentage of the sulfur input) are plotted in Fig. 3. The sulfur retention increased from ∿78% to 96-99% as the temperature was increased from 1325°F to 1450°F, then decreased to ∿60% as the temperature was further increased to 1650°F.

In contrast, with Illinois coal, a different batch of No. 1359 limestone (490-μm particle size), a gas velocity of ∿3 ft/sec, and at a lower Ca/S ratio of 2.5, the optimum temperature was 1550°F (ANL/ES/CEN-1002, p. 35) as shown in the curve also plotted in Fig. 3. The shift in peak temperature could be caused by the different characteristics of the coals, Ca/S ratios, or an unknown factor.

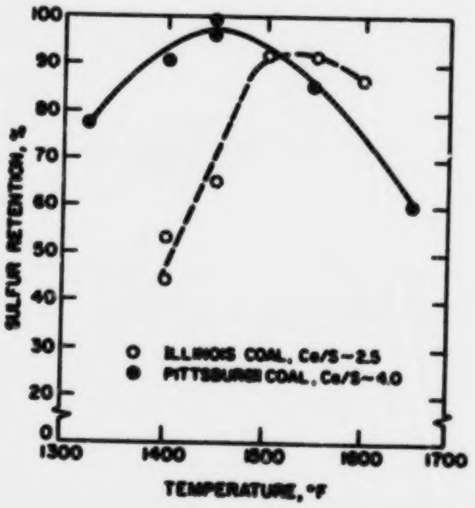

Fig. 3. Effect of Fluidized-Bed Temperature on Sulfur Retention

Gas Velocity = ∿3 ft/sec
Limestone size with Illinois coal: 490 μm
Limestone size with Pittsburgh coal: 609 μm

TABLE 1. Average Operating Conditions and Flue Gas Compositions for Bench-Scale Runs

	TYPE OF		FEEDRATES		CA/S	BED	BED	GAS	STEADY STATE FLUE GAS CONC. (DRY)					
EXP. NO.	COAL	ADD.	COAL.	ADD..		HEIGHT.	TEMP.	VEL.	O2.	CO2.	NO.	SO2.	CH4.	CO.
	---	---	#/HR	#/HR		IN.	F	FT/SEC	V/O	V/O	PPM	PPM	PPM	PPM
BC-7	2	1	5.4	1.8	2.30	24	1600	2.80	0.0	0.0	220	840	296	2040
BC-8	2	1	4.3	1.6	2.50	24	1600	2.80	0.0	0.0	320	800	72	3525
BC-9	2	6	4.1	1.7	2.30	24	1600	2.70	0.0	0.0	400	1100	113	1000
BC-10A	2	7	4.3	2.6	2.20	24	1600	2.90	0.0	0.0	250	800	82	870
BC-10B	2	7	4.3	2.6	2.20	24	1480	2.80	0.0	0.0	180	420	82	870
BC-10C	2	7	4.3	2.6	2.20	24	1800	3.20	0.0	0.0	300	3650	82	870
AR-1A	2	1	4.6	1.7	2.50	24	1400	2.50	0.0	0.0	250	2570	230	4200
AR-1B	2	1	4.6	1.7	2.50	24	1450	2.70	0.0	0.0	280	1460	180	4000
AR-1C	2	1	4.6	1.7	2.50	26	1500	2.80	0.0	0.0	420	420	70	3050
AR-1D	2	1	4.6	1.7	2.50	24	1550	2.90	0.0	0.0	420	420	40	3100
AR-1E	2	1	4.6	1.7	2.50	24	1600	2.80	0.0	0.0	440	700	50	3200
AR-1F	2	1	4.6	1.7	2.50	24	1400	2.60	0.0	0.0	260	2450	230	4200
AR-2A	2	1	4.3	1.6	2.60	24	1550	2.80	0.0	0.0	390	470	282	2050
AR-2B	2	1	4.4	1.7	2.60	24	1550	2.50	0.0	0.0	350	730	282	2050
AR-2C	2	1	4.5	1.7	2.60	26	1550	2.40	0.0	0.0	300	1250	282	2050
AR-2D	2	1	4.5	1.8	2.60	24	1550	3.10	0.0	0.0	430	850	282	2050
AR-4	3	1	4.2	1.6	2.80	24	1550	2.80	0.0	0.0	310	750	150	2000
AR-5A	3	1	3.8	1.6	3.00	26	1550	2.80	0.0	0.0	370	1100	0	0
AR-5B	3	1	4.4	3.1	5.50	24	1550	2.80	0.0	0.0	350	200	100	1200
AR-5C	3	1	4.1	2.4	4.60	24	1550	2.80	0.0	0.0	440	160	150	1600
AR-5D	3	1	4.1	1.3	2.50	24	1550	2.80	0.0	0.0	330	720	170	1600
AR-6C	3	1	5.6	3.5	4.20	24	1550	7.40	0.0	0.0	470	1500	100	1700
AR-6D	3	1	10.2	5.3	4.10	24	1550	3.50	0.0	0.0	340	770	500	3000
AR-6E	3	1	13.8	7.4	3.80	24	1550	5.50	0.0	0.0	320	1250	700	4100
AMER-1	3	3	4.5	0.5	1.00	24	1470	2.50	0.0	0.0	240	2630	300	3750
AMER-3	3	3	4.6	1.6	2.80	24	1470	2.50	0.0	0.0	260	1120	700	3000
AMER-4	3	3	4.6	1.0	1.90	24	1470	2.60	0.0	0.0	220	1460	3000	0
BRIT-1	4	4	5.0	0.4	2.10	24	1470	2.50	0.0	0.0	350	320	600	3200
BRIT-2	4	4	4.9	0.7	3.50	24	1470	2.60	0.0	0.0	310	250	200	0
BRIT-3	4	4	5.2	0.2	1.10	24	1470	2.60	0.0	0.0	265	660	300	4000
AMER-BRIT	3	4	4.6	1.0	1.80	24	1470	2.60	0.0	0.0	250	1300	200	3150
BRIT-AMER	4	3	5.2	0.4	1.80	24	1470	2.60	0.0	0.0	265	500	0	4800
AMER5C	3	3	5.2	1.8	2.99	24	1552	2.64	0.8	17.6	214	1516	3298	5000
AMER-5D	3	3	5.4	1.8	2.94	24	1544	2.64	2.6	19.3	264	1195	1674	3006
AMER-33	3	3	4.5	1.5	2.86	24	1476	2.63	2.5	16.3	252	888	1371	3200
AMER-8A	3	3	5.0	2.3	3.99	14	1545	2.85	2.8	16.2	348	891	370	200
AMER-8B	3	3	4.8	2.4	4.28	24	1560	2.98	2.6	16.9	279	751	497	720

TABLE 1 (Contd.)

EXP. NO.	TYPE OF		FEEDRATES		CA/S	BED	BED	GAS	STEADY STATE FLUE GAS CONC. (DRY)					
	COAL	ADD.	COAL.	ADD.,		HEIGHT.	TEMP.	VEL.	O2.	CO2.	NO.	SO2.	CH4.	CO.
	---	---	#/HR	#/HR		IN.	F	FT/SEC	V/O	V/O	PPM	PPM	PPM	PPM
AMER8-C	3	3	5.0	2.3	3.98	46	1553	3.15	3.0	16.4	352	570	422	200
HUMP-1A	5	3	4.1	1.3	4.18	24	1441	2.60	3.0	0.0	464	25	180	300
HUMP-1B	5	3	4.2	1.4	4.30	24	1548	2.77	0.0	0.0	529	380	283	200
HUMP-1C	5	3	4.1	1.4	4.45	24	1650	2.83	0.0	0.0	610	980	192	250
HUMP-1D	5	3	3.8	1.3	4.58	24	1455	2.62	3.0	0 0	529	64	200	500
HUMP-1D	5	3	4.8	1.5	4.20	24	1459	2.63	3.1	16.3	493	85	344	500
HUMP-1E	5	3	4.0	1.3	4.44	24	1395	2.42	3.3	16.4	447	276	449	1200
HUMP-1E	5	3	4.0	1.3	4.32	24	1319	2.50	3.1	15.5	338	480	701	1200
HUMP-2A2	5	3	4.0	0.8	2.67	24	1456	2.61	2.2	16.2	336	564	549	1000
HUMP-2B3	5	3	4.1	0.3	1.00	24	1443	2.57	3.7	15.6	461	1310	250	800
HUMP3	5	3	4.0	0.3	1.10	24	1452	2.53	2.8	15.6	486	1500	259	1000
HUMP-3-2	5	3	4.0	0.4	1.28	24	1446	2.52	3.0	15.3	534	1526	449	1500
HUMP-4-1	5	3	4.0	0.6	2.00	24	1464	2.55	10.4	16.5	531	1571	773	2900
HUMP-4-2	5	3	4.0	0.3	0.94	24	1441	2.51	3.1	15.9	506	1480	538	2100
HUMP-4-3	5	3	4.1	0.3	1.00	24	1443	2.50	3.3	15.2	433	1413	550	2000
HUMP-4-4	5	3	4.0	0.4	1.46	24	1448	2.52	3.4	14.8	396	1306	697	2200
HP-5-A	5	0	4.0	0.0	0.00	24	1325	2.40	0.0	16.7	462	1910	720	4400
HP-5-B	5	0	3.9	0.0	0.00	24	1450	2.79	0.0	0.0	609	1911	527	3000
HP-5-C	5	0	3.6	0.0	0.00	24	1538	2.90	0.0	16.5	626	2057	880	4500
HP-5-D	5	0	4.2	0.0	0.00	24	1605	2.99	0.0	16.7	601	2231	842	3400
HP-5-E	5	0	4.3	0.0	0.00	24	1325	2.70	0.0	0.0	585	1987	800	5300
HP-6-A	5	0	4.4	0.0	0.00	24	1328	2.59	2.0	16.3	600	2282	754	0
HP-6-B	5	0	4.0	0.0	0.00	24	1439	2.73	2.0	16.7	684	2119	577	0
HP-6-C	5	0	4.4	0.0	0.00	24	1544	2.87	1.4	16.7	684	2289	1003	0
HP-6-D	5	0	5.0	0.0	0.00	24	1642	3.04	1.2	16.7	642	2452	1319	0
PBY-2-A	3	0	4.4	0.0	0.00	24	1326	2.40	2.1	15.5	534	3903	460	4400
PBY-2-B	3	0	4.1	0.0	0.00	24	1450	2.60	3.2	15.4	646	3677	165	1500
PBY-2-C	3	0	4.2	0.0	0.00	24	1551	2.70	2.9	0.0	654	3759	174	1500
PBY-2-D	3	0	4.3	0.0	0.00	24	1644	2.80	2.7	15.7	649	4095	400	2500
PBY-2-E	3	0	4.2	0.0	0.00	24	1450	2.60	0.0	0.0	672	3733	60	1000
PEABY-4	3	3	4.0	2.1	4.54	24	1479	2.61	3.3	15.1	5	4637	98	600
PEABY-5	3	3	3.9	1.2	2.58	24	1547	2.70	3.2	15.4	318	452	349	400
PEABODY-5R	3	3	3.9	1.1	2.43	24	1550	2.69	3.4	15.0	294	649	372	500
PEABY-6	3	3	4.0	1.3	2.89	24	1551	2.68	3.1	15.6	388	1169	624	1500
PEABODY-6R	3	3	3.9	1.1	2.43	24	1550	3.01	0.0	15.5	236	845	200	63
AMER-333	3	3	4.3	1.7	3.50	24	1471	2.79	2.3	16.7	121	660	786	135
AMER 333-3	3	3	4.7	1.5	2.75	12	1468	2.59	2.2	17.2	494	1459	22	3569
AMER 333-4	3	3	5.0	1.5	3.25	12	1477	2.56	2.7	17.8	203	1172	266	3630

TABLE 1 (Contd.)

NOTE THAT A "0000" OR A "-10" OR A "0.0" (IN O2 AND CO2 CONC.) INDICATETHAT DATA EITHER HAVE NOT BEEN TABULATED OR ARE NOT AVAILABLE

Additional Notes:

1. Only data from combustion runs are tabulated. If the data logger was not in operation during a run, no data from that run are listed.
2. Some numbers in this table differ from those reported in the text. This sometimes is caused by a rounding-off procedure but is more often caused by a malfunction of the data logger. These malfunctions have gradually been corrected as the system has been used.
   An example of a malfunction has been the printing of "1's" instead of "7's". Numbers are obtained every five minutes during a run and are averaged to obtain, for example, the average bed temperature during a run. If the numbers averaged include incorrect numbers, an error results. However, the plotted data for each run have been examined, and the correct average number has been used in the text.
3. In the "coal" column, "2" represents Illinois coal, shipment 2; "3" represents Illinois coal, shipment 3; "4" represents British coal; and "5" represents Pittsburgh coal. In the "additive" column, "1" represents limestone No. 1359, shipment 1; "2" represents limestone No. 1359, shipment 2; "4" represents British limestone; "6" represents limestone No. 1360; and "7" represents Dolomite No. 1337.

b. Ca/S Mole Ratio in the Feed. Additional experiments have been done to investigate the effect on sulfur retention of Ca/S mole ratio in the solids feeds. The additive types, coals, and operating conditions used differed from those studied in earlier work. The effect of Ca/S ratio is shown (Fig. 4) for the Pittsburgh and the Illinois coals at the fluidized-bed temperature where sulfur retention had been maximized—1450°F for the Pittsburgh coal and 1550°F (some 1600°F data are included also) for Illinois coal. Additional data on the effect of Ca/S ratio on sulfur retention were obtained during combustion experiments in which data from the ANL 6-in.-dia combustor were compared with data from the British 6-in.-dia combustor (these experiments are discussed below).

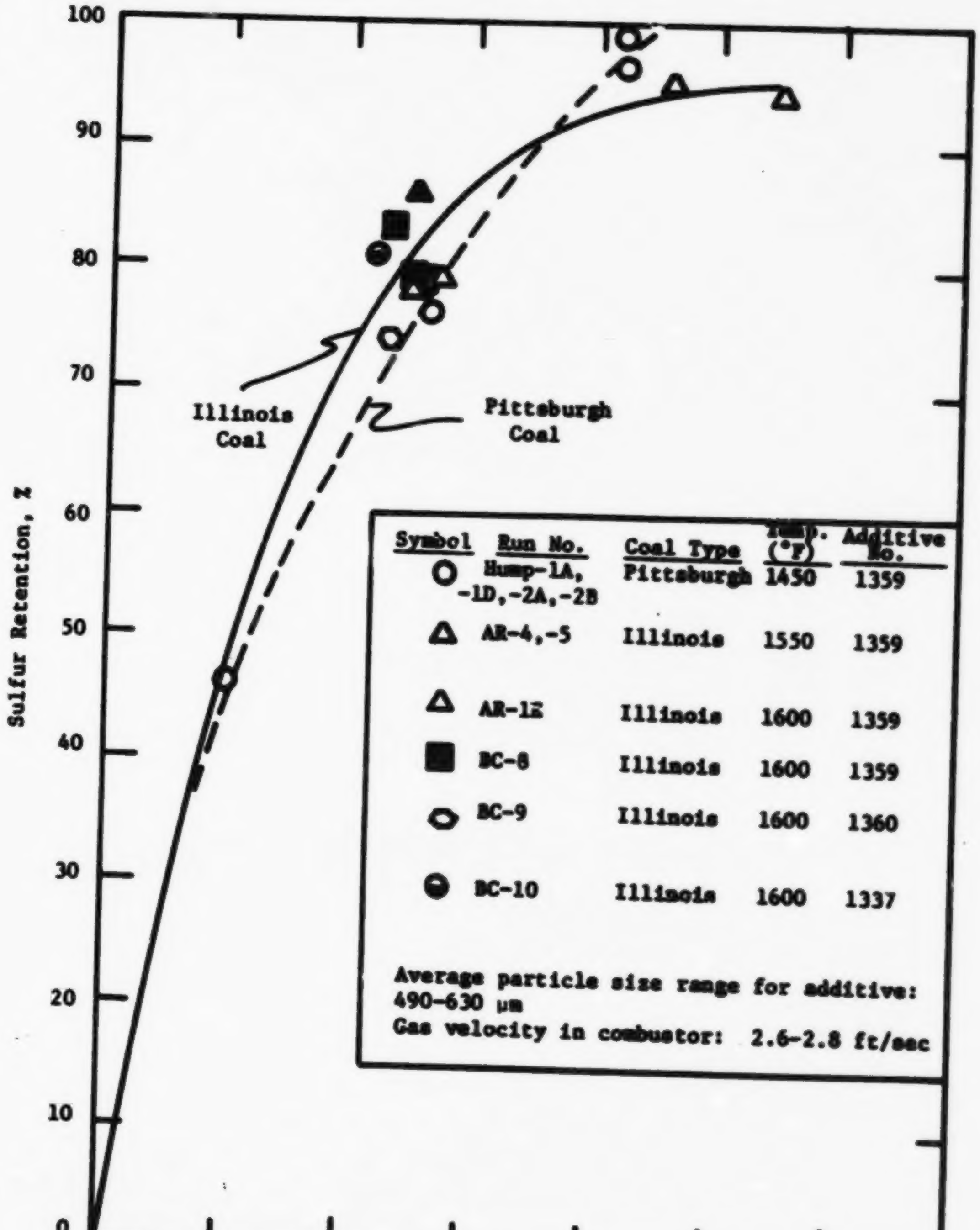

Fig. 4. Sulfur Retention as a Function of Ca/S Mole Ratio in the Feed

Four runs (Hump-1A, -1D, -2A, and -2B) were performed with Pittsburgh coal and 609-μm limestone No. 1359, a 1450°F fluidized-bed temperature, a gas velocity of 2.2-3.7 ft/sec, and Ca/S ratios of 1.0 to 4.6 in the feed. The sulfur retention increased from ~46% at a Ca/S ratio of 1 to 75% at a Ca/S ratio of 2.7, and to 96% at a Ca/S ratio of 4.2-4.6.

Experiments AR-5B to -5D were completed at 1550°F with 490-μm limestone No. 1359 and Illinois coal containing 3.7% S (dry basis) to study the effects on sulfur retention of Ca/S mole ratios in the feed streams of 2.5, 4.6, and 5.5. Sulfur retentions were 78, 95, and 94%, respectively, as shown in Fig. 4.

The effect of Ca/S mole ratio was also examined in experiments carried out in the 6-in.-dia ANL combustor and a 6-in.-dia combustor at the Coal Research Establishment (CRE) laboratories (at England) to determine if SO_2 removals would differ significantly when the two combustors were operated under similar conditions. Three limestone stoichiometric addition levels were used in experiments with (1) American coal and limestone fed separately, (2) premixed American coal and limestone, (3) British coal and American limestone, (4) British coal and limestone, and (5) American coal and British limestone (Table 2). The British coal and limestone were Welbeck coal and a limestone furnished by J. Gregory & Son. The American coal and limestone were Peabody Mine 10 coal and limestone No. 1359. The sulfur retention data in Fig. 5 (presented as ppm SO_2 in the flue gas) indicate that sulfur retention increased at higher Ca/S mole ratios for British and American coal-limestone combinations in both combustors.

c. Type of Coal. The effect of type of coal on sulfur retention could not be evaluated because of insufficient data. However, at bed temperatures of 1450-1470°F and retentions of less than 90%, the sulfur retentions are not much different for Illinois and Pittsburgh coals (Fig. 6). Data are not available for comparing sulfur retentions at a bed temperature of 1550°F. No data on sulfur retentions above 90% are available for Illinois coal at 1450°F.

Sulfur retentions obtained in experiments Hump-1A, -1D, -2A, and -2B, in which Pittsburgh coal was burned in the ANL combustor with limestone No. 1359 additive, are plotted in Fig. 6 along with sulfur retentions for earlier ANL work with Illinois coal and limestone No. 1359 additive (Amer-6, -3, -33, -4, and -1). Also plotted are sulfur retention data for British experiments[1] at the Coal Research Establishment laboratories, in which Illinois coal was burned in the CRE 6-in.-dia fluidized-bed combustor with limestone No. 1359 additive. The fluidized-bed temperature was nearly the same (1450 to 1472°F) in all of these runs. Below 90% retention, the data from the various experiments fell along a smooth curve, indicating that at ~1450°F with limestone No. 1359 additive, sulfur retention was independent of the source of coal. Zielke et al.[2] had reported sulfur retention to be independent of the source of coal when Disco char (3.7 wt % S), Cresap char (1.2 wt % S), and Ireland coal (1.3 wt % S) were burned in a fluidized bed of Tymochtee dolomite at 1800°F.

TABLE 2. Operating Conditions and Results for British-American Experiments Performed at ANL

Equipment:	ANL 6-in. dia Fluidized-Bed Combustor
British Coal:	Welbeck, 1.2 wt % S
American Coal:	Illinois, 3.7 wt % S
British Additive:	British limestone, Stoke-on-Kent, 94.6 wt % $CaCO_3$
American Additive:	No. 1359 limestone, 94.8 wt % $CaCO_3$
British Starting Fluidized Bed:	Welbeck Coal Ash (from British combustor)
American Starting Fluidized Bed:	Calcined and partially sulfated No. 1359 limestone
Temperature:	1470°F

Expt.	Run Time (hr)	Coal (lb/hr)	Additive (lb/hr)	Ca/S Mole Ratio[a]		Superficial Gas Velocity (ft/sec)	Flue Gas Composition					Sulfur Retention (%)	Utiliz. of CaO in Additive Feed (%)
				A	B		O_2 (vol %)	SO_2 (ppm)	NO (ppm)	$CO+CH_4$ (ppm)	CO_2 (vol %)		
						British Coal - British Additive							
Brit-1	14	5.0	0.42	2.1	2.3	2.5	2.9	320	350	4200	16.0	78	37
Brit-2	6.5	4.9	0.69	3.5	3.8	2.6	3.0	250	310	b	16.3	82	23
Brit-3	8	5.2	0.23	1.1	1.3	2.6	2.4	660	265	>5500	16.2	55	50
						American Coal - American Additive							
Amer-1	39	4.5	0.53	1.0	1.1	2.6	2.7	2480	240	4050	16.0	38	38
Amer-3	21	4.6	1.6	2.8	3.0	2.6	2.5	870	260	3700	16.5	78	28
Amer-4	13	4.6	1.05	1.9	2.0	2.6	3.1	1460	215	3000	16.2	63	33
Amer-33	6.5	4.6	1.5	2.7	2.8	2.6	2.5	840	240	3600	16.8	79	29
						American Coal - British Additive							
Amer-Brit	8	4.6	1.0	1.8	2.0	2.6	2.6	1300	250	2400	16.2	68	38
						British Coal - American Additive							
Brit-Amer	4	5.2	0.38	1.8	2.0	2.6	2.4	~500	265	4800	16.4	~66	37

[a] Column A includes only the calcium in the limestone feed; column B includes the calcium in the limestone feed and the coal.

[b] CO concentration not known for this experiment, CH_4 = 200 ppm.

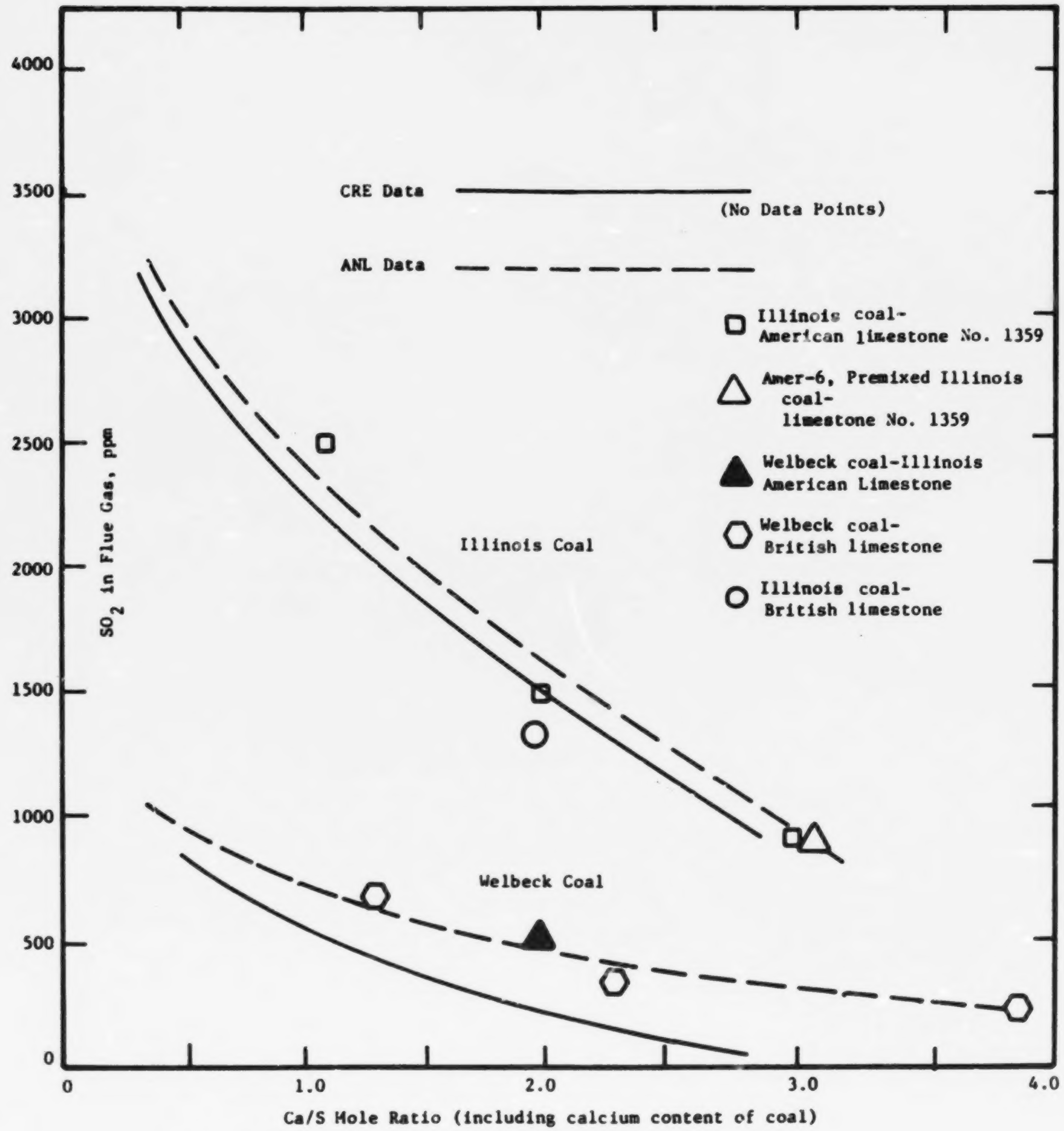

Fig. 5. SO_2 Concentrations in Flue Gas for ANL and CRE Combustion Tests with American and British Coal-Limestone Combinations

Gas Velocity: ∿2.6 ft/sec
Fluidized Bed Temp.: 1470°F
Bed Height: 24 in.

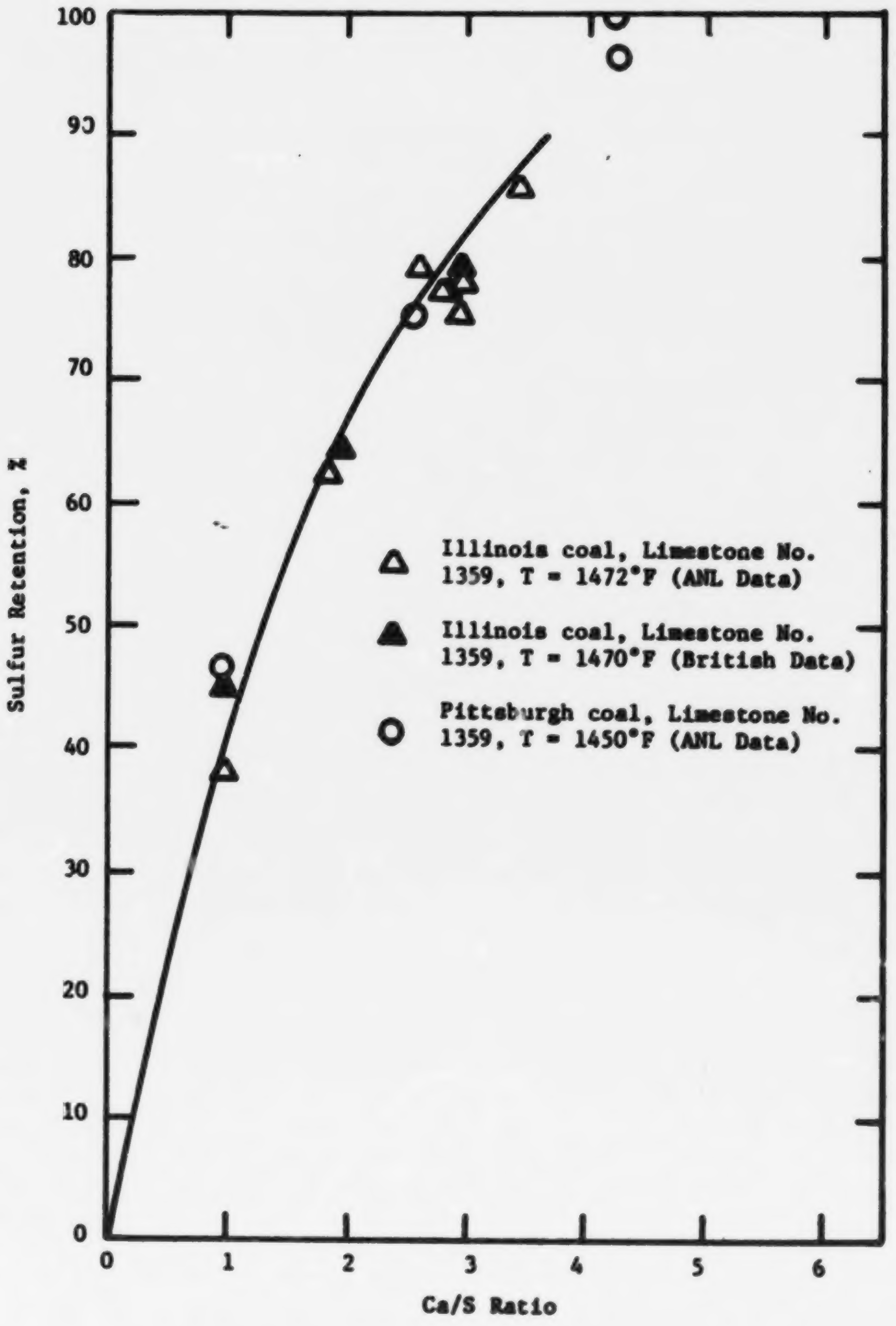

Fig. 6. Effect of Ca/S Ratio on Sulfur Retention for Three Series of Runs (Combustion of two coals in ANL combustor, one coal in British combustor)

d. Coal Particle Size. To determine the effect of particle size of the coal feed on sulfur retention, two experiments (PB-5R and PB-6R) were completed with -12 +50 mesh and -50 mesh Illinois coal. To ensure uniformity of all of the properties except size, the coal for both experiments was from the same batch of coal. The batch was crushed and screened, and the -12 +50 mesh fraction was divided into two portions. One portion was fed during PB-5R and the remaining portion was crushed to obtain the -50 mesh coal fed in PB-6R. Other experimental conditions were selected (a Ca/S mole feed ratio of 2.4 and a fluidized-bed temperature of 1550°F) to give moderate retention of sulfur so that the effect of particle size, if any, would be clearly indicated.

It was expected that most of the -12 +50 mesh particles would be burned within the fluidized bed and that some of the -50 mesh coal would burn in the zone above the fluidized bed (where SO_2 absorption by limestone would be less efficient). In earlier work, it has been observed that stratification of particles can occur in the bed to some extent for particle size distributions similar to that used in experiment PB-5R. The larger-sized particles of coal are probably burned close to the bottom of the bed and the SO_2 released is sorbed by CaO at a bed level above the burning site. Sulfur retentions by limestone additive were 81% and 75%, respectively, in PB-5R and -6R.

These sulfur retentions were compared with that obtained in experiment AR-5D, in which Illinois -14 mesh coal was burned under operating conditions nearly identical to those used in the above experiments. The particle sizes for the -14 mesh coal included most of the particle sizes present in the other two fractions. Sulfur retention in experiment AR-5D was 78%. Thus, similar sulfur retentions were obtained by burning coal of three particle size distributions. Nevertheless, the results indicate a small benefit from burning coarse coals or coals containing small amounts of fine particles.

e. Additive Type. The SO_2 removals for runs performed at a Ca/S mole ratio of 2.5 and fluidized-bed temperatures of 1550 or 1600°F with several types of additives may be compared in Fig. 4. With limestone No. 1359 and dolomite No. 1337, sulfur retention was 75-85% indicating that differences in these additive types had only minimal effects at these temperatures.

Experiments performed at the Coal Research Establishment and ANL allowed comparison of the relative reactivities of British and American limestones for SO_2 removal. Illinois coal and British Welbeck coal were each fed with 609-μm limestone No. 1359 and 555-μm British limestone. Figure 5 shows that in the tests with Illinois coal, the British limestone apparently was more effective for removing SO_2 from the flue gas than was limestone No. 1359. In tests with Welbeck coal, the SO_2 levels in the flue gas were about the same for limestone No. 1359 and British limestone--probably within the experimental error.

f. Additive Particle Size. Sulfur retention in AR-6 (which used 1000-μm limestone No. 1359 and a Ca/S ratio of 4) was compared with sulfur retention in experiments AR-5, BC-8, BC-9, and BC-10 (which used limestones No. 1359 and 1360 and dolomite No. 1337 of 490-630 μm average diameter, a superficial gas velocity of 3 ft/sec, and a Ca/S of 2.2-5.5). Sulfur retention in AR-6 was measured at gas velocities of 3.5-7.4 ft/sec, and the sulfur retention at 4 ft/sec was based on extrapolation of experimental values. Sulfur retention was calculated to be ~87% for the larger particle additive and 93% for the smaller particle at a Ca/S ratio of 4.0. This suggests that additive particle size, at least in the region of high sulfur retention, has only a moderate effect on sulfur retention at a particular fluidizing-gas velocity.

g. Fluidized-Bed Height. The effect of the height of a fluidized bed on the percentage of sulfur retained in the bed was studied in one-stage combustion runs. In Amer-8A, -8B, and -8C performed under similar conditions except that bed heights were 14, 24, and 46 in. [length to diameter (L/D) ratios of 2.3, 4.0, and 7.7], the sulfur retentions were 78, 80, and 83 (Table 1), respectively, indicating a minor effect of bed height. At the highest L/D ratios, solids slugging was severe. This did not affect sulfur retention, but operation of the combustor was difficult--heat transfer was poor, and high feed rates of coal were noted several times that caused variations in the SO_2 concentration in the flue gas.

h. Superficial Gas Velocity. Increased sulfur retention with decreased superficial gas velocity (in the range of 3.5 to 7.4 ft/sec) was observed in experiment AR-6, in which the operating conditions were a coal combustion temperature of 1550°F, a starting bed of partially sulfated limestone No. 1359, and addition of limestone No. 1359 (>1000 μm particle size) and Illinois coal at a Ca/S mole feed ratio of ~4. The relatively coarse additive was selected to ensure that additive particles would be retained in the fluidized bed at high gas velocities. At gas velocities of 3.5, 5.5, and 7.4 ft/sec, the average SO_2 concentrations in the flue gas were 770, 1250, and 1500 ppm, corresponding to retentions of 83, 73, and 66% of the sulfur fed to the reactor (Table 1). These data are also shown in the semilog plot of Fig. 7 and may be correlated with the equation:

$$R = 101.79\, e^{-0.0625\, v} \qquad (1)$$

where R = SO_2 removal, %

v = superficial gas velocity, ft/sec

Previous ANL data (SACC-8 and -9, ANL/ES/CEN-1002, p. 26) for 25-μm No. 1359 limestone additive, coal combustion at 1600°F, and alumina fluidized beds do not show the same correlation between sulfur retention and gas velocity for gas velocities of 2.7 and 8.6 ft/sec. Similarly, in tests carried out by Pope, Evans, and Robbins using <44 μm No. 1359 limestone, a Ca/S ratio of ~2, a sintered coal-ash fluidized bed, and a combustion temperature of 1525 to 1600°F,[3] gas velocity in the range 6.0 to 12.8 ft/sec had essentially no effect on sulfur retention.

Other American and British data for series of coal combustion runs performed at several gas velocities and various Ca/S mole ratios have been examined to further elucidate the relationship between sulfur retention and superficial gas velocity. Results of recent British experiments[4] using Welbeck coal, 440-μm British limestone, Ca/S ratios of 1 and 2, and a coal-ash bed show that sulfur retention is greater at a gas velocity of 2 ft/sec than at 3 ft/sec (Fig. 7). The equations fitted to the two experimental points at each stoichiometric Ca/S ratio are:

$$R = 100.4\ e^{-0.071\ v} \qquad Ca/S = 2 \qquad (2)$$

and

$$R = 102.1\ e^{-0.266\ v} \qquad Ca/S = 1 \qquad (3)$$

To allow further comparison, Fig. 7 includes a datum point from a curve (Fig. 4) for limestone fluidized beds at 1550°F, a Ca/S ratio of 4, limestone and dolomite additives, and a gas velocity of ~3 ft/sec.

The slopes represented by equations 1, 2, and 3 decrease as the Ca/S ratios increase; thus, at sufficiently high Ca/S ratios, sulfur retention may be essentially independent of superficial gas velocity.

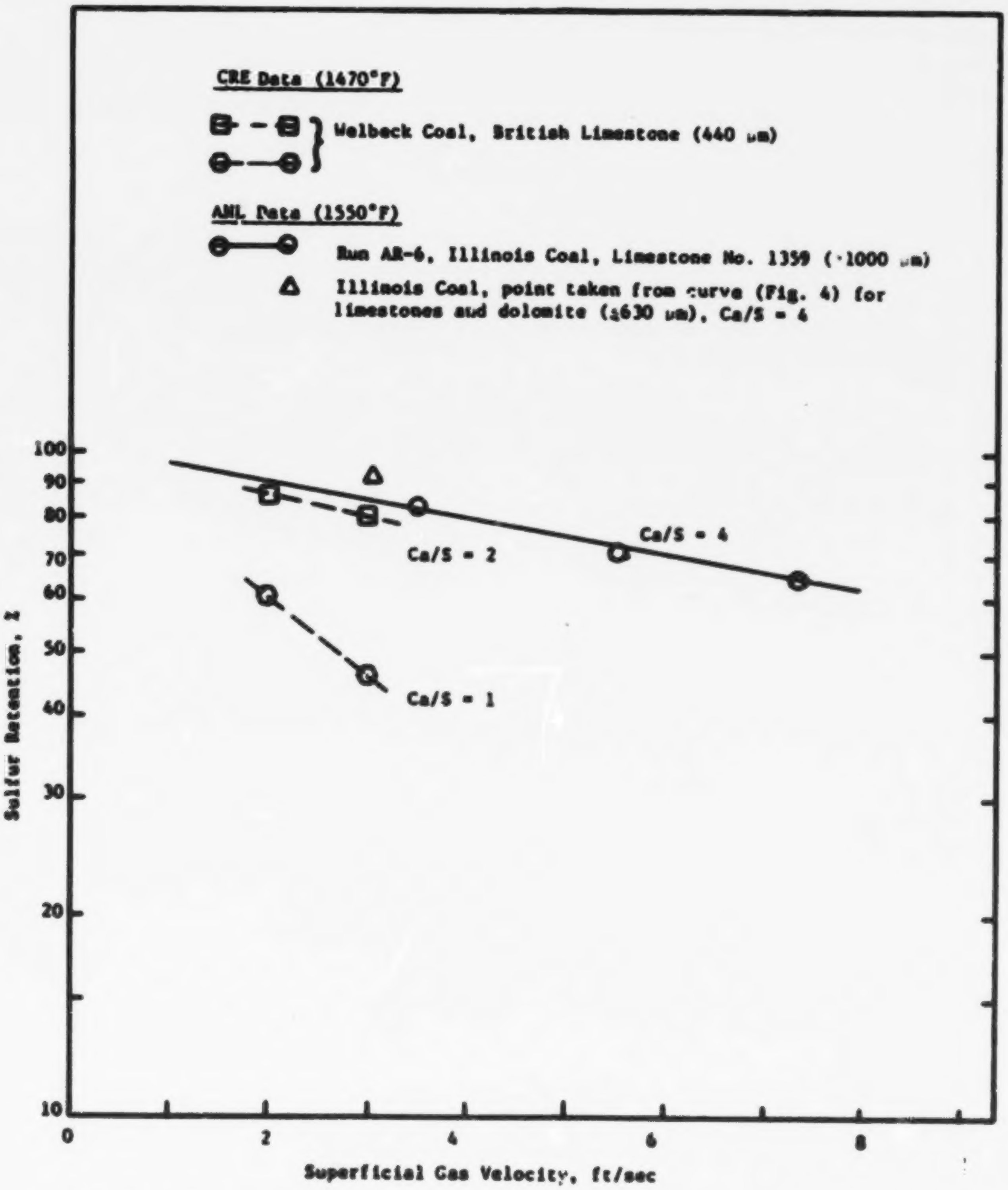

Fig. 7. Effect of Superficial Gas Velocity on Sulfur Retention

i. Excess Air. Runs to determine the effects of excess air (or oxygen) in the combustion gas on sulfur retention utilized Illinois coal, limestone No. 1359 additive, and a starting bed of partially calcined and sulfated limestone. Experiments Amer-5C, -5D, and -5E (at 1550°F) were performed at three excess air levels. The oxygen level in the off-gas was varied by adding pure oxygen at several rates to the fluidizing air before it entered the preheater. The purpose of adding oxygen in preference to air was to maintain the fluidizing-gas velocity essentially constant, since this variable affects sulfur retention.

Data from experiment Amer-5 are summarized in Table 3 and Fig. 8. In experiments Amer-5C, -5D, and -5E, the SO_2 level in the flue gas decreased from 1540 ppm with 0.7 vol % O_2 in the flue gas to 1350 ppm with 2.4 vol % O_2, and to 1170 ppm with 5.6 vol % O_2. Sulfur retentions were 67, 71, and 75%, respectively. Apparently, oxygen concentration slightly affects the reaction of SO_2 with limestone, and sulfur retention can be expected to increase when oxygen concentration in the flue gas is increased.

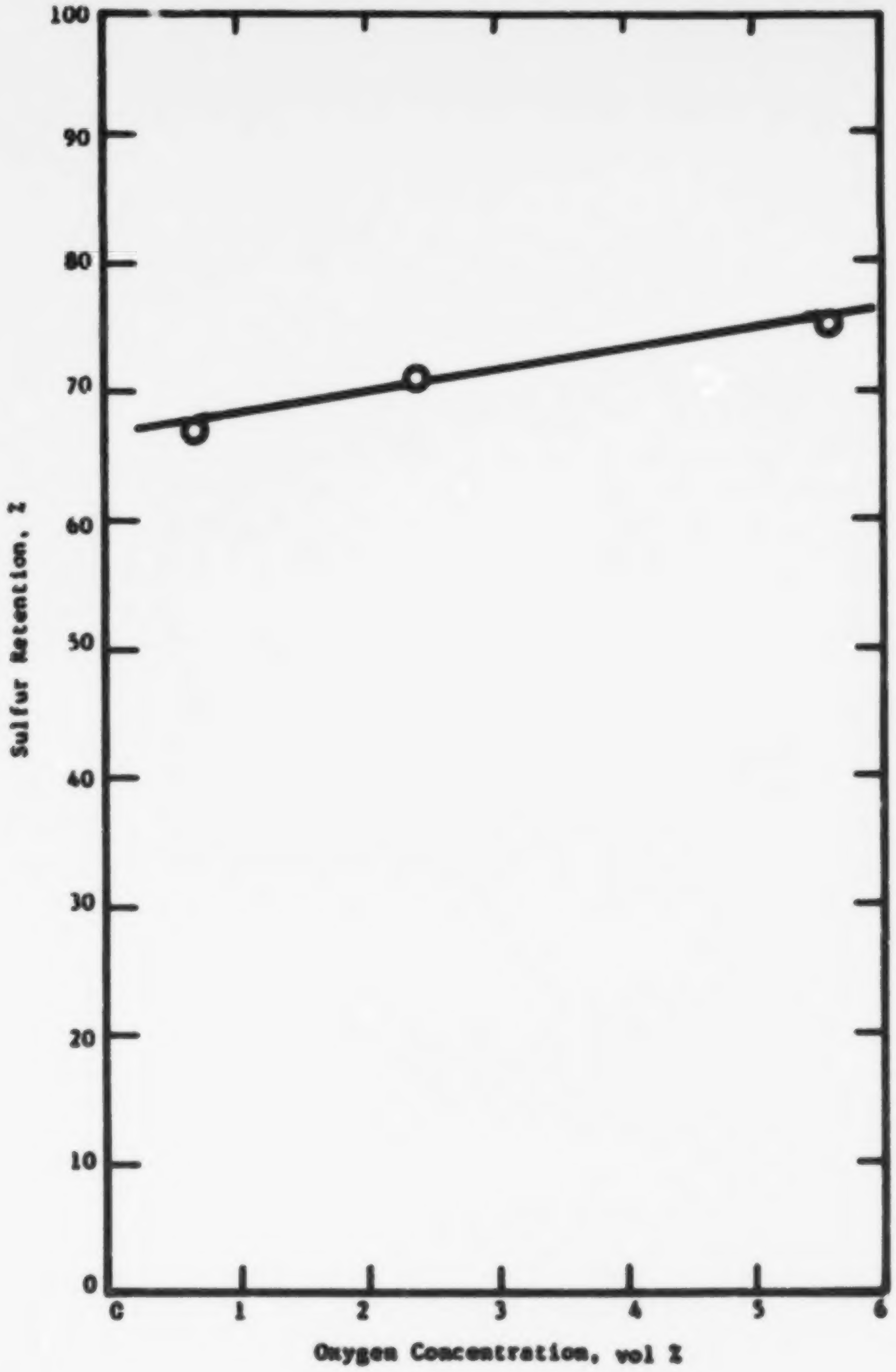

Fig. 8. Effect of Excess Oxygen in Combustion Air on Sulfur Retention, Experiments Amer-5C, -5D, and -5E

Ca/S Mole Ratio: ~2.8
Fluidized-Bed Temp.: 1550°F
Superficial Gas Velocity: 2.6 ft/sec

TABLE 3. Effect of Excess Oxygen in Combustion Air on Sulfur Retention

Equipment: ANL 6-in.-dia fluidized-bed combustor

Coal: Illinois Seam No. 6 (Peabody-Commonwealth Edison), 3.7 wt % S (-14 mesh)

Additive: Limestone No. 1359, as received (94.8 wt % $CaCO_3$, 0.9 wt % $MgCO_3$)

Starting Fluidized Bed: 18.0 lb partially sulfated and calcined limestone No. 1359 (609 μm) (~24-in. fluidized-bed depth)

Fluidized-Bed Temperature: 1550°F (Amer-5)

Expt. Amer-	Time at Equilibrium (hr)	Feed Rates		Ca/S[a] Mole Ratio	Superficial Gas Velocity (ft/sec)	Sulfur Retention (%)	CaO Utilization (%)	Flue Gas Composition[b]		
		Coal (lb/hr)	Additive (lb/hr)					O_2 (vol %)	SO_2 (ppm)	CO_2 (vol %)
5C	7.5	5.2	1.8	2.8	2.6	67	24	0.7	1540	17.8
5D	4.5	5.2	1.8	2.8	2.6	71	25	2.4	1350	>19.3
5E	5.5	5.0	1.8	2.9	2.6	75	26	5.6	1170	19.6

[a] Values do not include calcium content of coal, which would have increased Ca/S by ~0.1.

[b] The concentrations of the components in the flue gas in Runs 5D and 5E should not be compared with similar data from other runs made to date. In these two runs the excess oxygen requirements were supplied by oxygen rather than air, resulting in a smaller volume of gas than if air had been used. Consequently, the measured flue gas concentrations are proportionately higher.

j. Moisture Content of Coal. In a run to determine the effect of moisture content of the coal on sulfur retention, Pittsburgh coal was fed at 4 lb/hr, limestone No. 1359 was fed at 0.3 lb/hr, and water was added at different rates to the fluidizing air (at the base of the ANL 6-in.-dia combustor). The fluidized-bed temperature was maintained at 1450°F, the fluidizing gas velocity at 2.6 ft/sec, and the Ca/S ratio at 1. The starting bed for this run (Hump-4) consisted of partially calcined and sulfated limestone No. 1359. The rate of water addition and the concentrations of flue gas components are listed in Table 4. The water injection rates were equivalent to burning coal with moisture contents up to 51 wt %.

The concentration of SO_2 in the flue gas remained the same (~1400 ppm) throughout the run. The concentrations of CH_4 and CO in the flue gas decreased upon the addition of moisture, but did not decrease further with increased rate of addition. The NO concentration decreased as well, as discussed in Section II.D.2.

TABLE 4. Effect on Flue Gas Composition of Addition of Moisture to the Fluidized Bed, Run Hump-4

Coal: Humphrey (Pittsburgh) coal,
Morgantown, W. Va., 2.4 wt % S

Additive: Limestone No. 1359

Fluidized-Bed Temperature: 1450°F

Ca/S Mole Ratio: 1.0

Gas Velocity: 2.6 ft/sec

Run Duration (hr)	Water Addition		Concentration in Flue Gas[a]					
	Volume Rate (cc/min)	Equivalent wt % water in coal	O_2 (vol %)	CO_2 (vol %)	CO (ppm)	CH_4 (ppm)	NO (ppm)	SO_2 (ppm)
1.25	0	1.8	2.2	16.5	2900	850	530	1400[b]
2.00	10	26.2	2.7	16.0	2100	580	510	1400[b]
2.00	20	40.8	3.3	15.0	2100	580	440	1400[b]
2.00	30	50.6	3.4	15.0	2100	580	380	1400[b]

[a] Moisture-free basis.

[b] Reduction in SO_2 emission = 42%.

k. Solids Feeding Method. An experiment (Amer-6) was made in which coal and limestone were premixed before being fed to the combustor rather than being fed separately. This change had little effect on the sulfur retention, which was similar for runs without premixing (see Fig. 5). Operating conditions were a temperature of 1470°F at a Ca/S ratio of 2.6, and a gas velocity of 2.6 ft/sec.

l. Temperature of Gas in the Freeboard. During the first half of Hump-3 with -14 mesh Pittsburgh coal and 609-μm limestone No. 1359, the upper section of the ANL fluidized-bed combustor was insulated; during the remainder of this run (Hump-3-2, Table 1), the upper section was not insulated (absence of insulation is normal for the ANL combustor) and was cooled by natural circulation of the ambient air. The temperature of the fluidized bed, where most of the coal was burned, was 1450°F for the entire run. The temperature of the upper section of the combustor was 1340°F during the first half and 1020°F during the remainder of the run. The Ca/S mole ratio was 1, and the gas velocity was ∿2.6 ft/sec.

The concentration of SO_2 in the flue gas was ∿1500 ppm during both periods, indicating that sulfur-removal reactions occurred essentially in the fluidized-bed zone. Upon removal of insulation of the upper section, the concentrations of CH_4 in the flue gas increased from 260 ppm to 450 ppm, that for NO from 490 to 540 ppm, and that for CO from 1000 to 1500 ppm. This indicates that gaseous combustion of CO, CH_4, and possibly additional reaction of CO with NO increased when the upper section of the combustor was insulated and the gas temperature reached 1340°F.

m. Absence of Additive. Currently, the results of combustion experiments are given as percent sulfur retained—the percentage of sulfur in the feed that does not appear as SO_2 in the flue gas. However, previous studies on combustion efficiency (ANL/ES/CEN-1002, Appendix D) indicate that some unburnt coal particles are elutriated with the ash. The unburnt carbon in the ash may contain some sulfur. Therefore, not all sulfur retained has been released as SO_2 and reacted with additive. To determine how much SO_2 and NO is actually released during combustion, experiments Hump-5A to -5E (Table 1) and PB-2A to -2E were performed with no additive present.

Five experiments (Hump-5A to -5E) were performed with -14 mesh Pittsburgh coal (2.4 wt % S), with no limestone injected, coal feed rates of about 4 lb/hr, and the fluidized-bed temperature ranging from 1325 to 1650°F. The duration of operation at each temperature was 1 to 1.5 hr. The fluidized bed contained refractory alumina as the major constituent and unelutriated ash as the minor constituent. The fluidized-bed depth was about 24 in., and the fluidizing-air velocity was 2.4 to 2.8 ft/sec. The observed concentrations of SO_2 were 150 to 300 ppm less than the values calculated by assuming that all sulfur in the coal had been converted to SO_2, as shown in the following tabulation.

	SO_2 (ppm)	Calc. SO_2 (ppm)	Bed Temp (°F)
Hump-5A	1900	2290	1325
-5B	1900	2210	1450
-5C	2040	2300	1550
-5D	2200	2360	1650
-5E	1960	2250	1325

When Illinois coal (3.7 wt % S) was burned under similar conditions in five experiments (PB-2A to -2E), the concentrations of SO_2 were higher, as expected due to the higher concentration of sulfur in this coal. The observed and calculated SO_2 concentrations were about the same in three cases and in the fourth and fifth runs the calculated concentrations were 17% less and 7% higher than the measured concentrations, as shown:

	SO_2 (ppm)	Calc. SO_2 (ppm)	Bed Temp (°F)
PB-2A	3950	3900	1325
-2B	3750	3750	1450
-2C	3750	3700	1550
-2D	4250	3550	1650
-2E	3650	3900	1450

2. Effects of Variables on Reduction in Emissions of NO During One-Stage Combustion

Nitrogen oxides, principally nitric oxide (NO), are formed during the combustion of fossil fuels. At 1600°F (a common temperature for fluid-bed combustion), the equilibrium concentration of NO as a result of the nitrogen fixation reaction, $1/2\ N_2 + 1/2\ O_2 \rightleftarrows NO$, varies from 50 to 200 ppm, depending on the oxygen concentration. However, during combustion of coal in the bench-scale combustor, nitric oxide levels of 400-800 ppm have been measured. A possible explanation for these high NO concentrations is that the nitrogenous content of the coal (1-1.5 wt % in U.S. coals) is the source of NO. This amount is sufficient to form several thousand ppm. The residence time in the combustor is not sufficient for decomposition to equilibrium levels.

In recent investigations, NO release during coal combustion in the absence of additive was studied, as well as the effect of moisture content of the coal on NO removal.

In five experiments with Pittsburgh coal (Hump-5A to -5E) and five with Illinois coal (PB-2A to -2E), the quantity of NO released when no additive was present in the bed was determined. Coal was burned in an alumina bed at different temperatures (1325-1650°F). The NO concentration in the flue gas ranged from 450 to 630 ppm:

	Fl.-Bed Temp (°F)	NO in Flue Gas (ppm)
Hump-5A	1325	450
-5B	1450	610
-5C	1550	630
-5D	1650	600
-5E	1325	570

The lowest NO concentration was obtained at the lowest bed temperature.

With Illinois coal, the NO concentrations ranged from 530 to 680 ppm, and again the lowest NO concentration was obtained at the lowest temperature.

	Fl.-Bed Temp (°F)	NO in Flue Gas (ppm)
PB-2A	1325	530
-2B	1450	650
-2C	1550	660
-2D	1650	650
-2E	1450	680

However, with either coal, no good temperature correlation could be made. The NO levels are higher than those expected if additive had been present, indicating that sulfated additive has a beneficial effect, reducing NO levels in the flue gas up to approximately 50%.

The effect of moisture content of the coal on NO level was studied in Hump-4, in which water was added at different rates to the fluidizing air, at the base of the combustor (Table 4). Pittsburgh coal and limestone No. 1359 were used. The fluidized-bed temperature was maintained at 1450°F and the Ca/S ratio at 1. A Calcomp plot of NO concentration in the flue gas during all of Hump-4 is shown in Fig. 9. The concentration of NO decreased from 530 ppm to 510 ppm upon adding 10 cc/min water (equivalent to 26 wt % water in the coal), and to 380 ppm when the rate of water addition was further increased to 30 cc/min (equivalent to 51 wt % water in the coal). Reductions in the NO concentration may be due to a catalytic effect of H_2O.

3. Effects of Variables on Chemical Composition and Physical Properties of Bed and Elutriated Materials

Samples from the fluidized bed and from elutriated material collected in the primary and secondary cyclone separators and the final filter were examined and analyzed. An electron microprobe was used to examine sulfur distribution in additive particles. The extent of limestone calcination and calcium utilizations were calculated from analyses of feed and product streams. The extent of hydration of partially sulfated limestone upon exposure to the atmosphere was measured. Elutriated material was analyzed for the presence of calcium sulfite, and particle size distributions of bed samples taken at intervals during a run were measured. Decrepitation of additive particles in the bed was calculated from calcium levels and size distributions of the fresh additive and of elutriated solids. Bulk and tapped densities of solids from the bed, cyclones, and final filter were also determined.

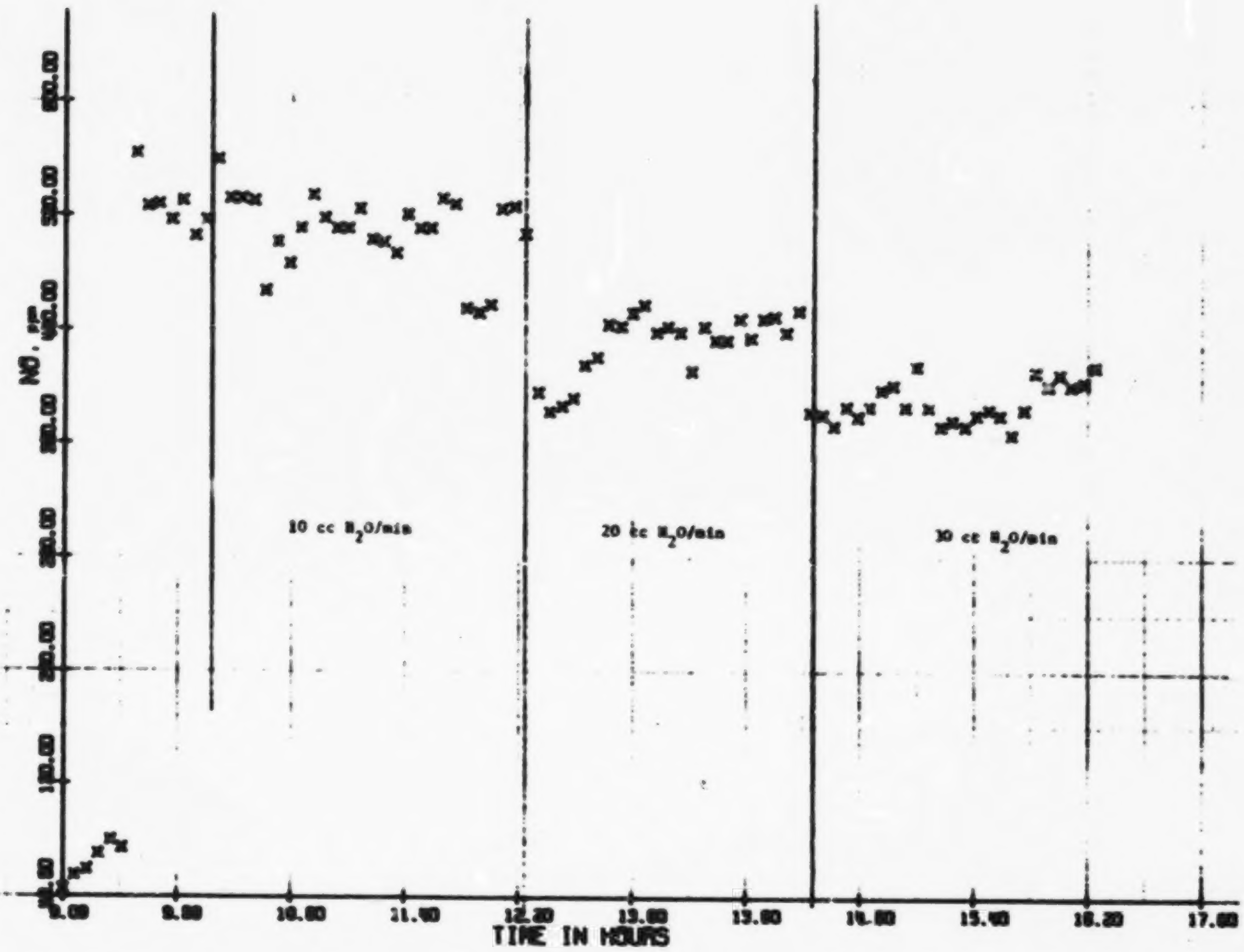

Fig. 9. Concentration of NO in Flue Gas during Hump-4 (Calcomp plot)

a. Effect of Type of Fuel on Sulfur Distribution in Additive Particles. The distribution of sulfur in bed and elutriated particles from bench-scale combustion experiments was determined with an electron microprobe, which offers nondestructive, in situ elemental analysis in micron-scale areas.

Two samples of elutriated material from the primary cyclone were examined.* One sample was from a coal combustion experiment, and the other was from a natural gas combustion experiment with SO_2 added from a separate source. Elutriated particles from the two samples showed differences in particle composition. For particles from the coal combustion experiment, the sulfur concentration usually was lower at a greater distance from the surface of the particle. For particles in samples from the natural gas experiment, sulfur concentrations appeared to be more uniform throughout

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[*] Examination performed by K. Natesan.

the particles. Few particles exposed to combustion of either fuel showed the calcium and sulfur levels that would be observed if CaO had been completely converted to $CaSO_4$. Some particles from the natural gas combustion experiment had the calcium concentration of $CaCO_3$, indicating that little calcination or sulfation had occurred. For these elutriated particles the residence time in the bed was relatively short as compared to particles remaining in the bed itself.

In samples removed from the bed, the distribution of sulfur across the cross section of most limestone and dolomite particles from coal combustion experiments was rather uniform. The possible relationship of this sulfur distribution pattern to the reaction mechanism was considered. The most probable mechanism for the CaO + SO_2 reaction, when it occurs under oxidizing conditions, is one in which the reaction initially proceeds in the surface layer of the particle, after which the SO_2 diffuses through the initially sulfated layer. Some of the particles examined did show higher sulfur concentrations at the surface, which would be expected for the shell-diffusion reaction mechanism. Although most of the bed particles came from experiments in which oxidizing conditions prevailed, both uniformly distributed and surface-concentrated sulfur were present. More detailed results are presented in Section IV of this report, Mechanism of Lime Sulfation Reaction.

b. Limestone Calcination. In some experiments analyses for calcium, sulfur, and occasionally $CO_3^=$ were performed on samples from the fluidized bed and from elutriated material. From the analyses, the extent of calcination and occasionally the Ca/S ratios for these materials were determined.

The extent of calcination of limestone material was determined for fluid-bed samples from experiments AR-6C, -6D, and -6E, performed to explore the possible effect on SO_2 removal at 1550°F of various superficial gas velocities. Illinois coal and 490-μm limestone No. 1359 were fed to a starting bed of partially calcined and sulfated lime to give a Ca/S mole ratio in the feed of ∿4.0. The average values of the extent of limestone calcination were 95.7, 94.5, and 97.3% for superficial gas velocities of 3.5, 5.5, and 7.4 ft/sec. These results show no direct relationship of the extent of calcination to the superficial gas velocity but indicate that calcination is rapid enough at 1550°F to be essentially independent of gas velocity with material of this particle size.

Calcination was essentially complete (90-100%) for fluidized-bed and final-filter solids and ranged from 60 to 84% for solids elutriated to the cyclones in the Amer and Brit experiments. The high calcination level of the fluidized-bed solids is accounted for by their long residence time in the combustor; the high calcination level of the limestone component of the final-filter material is probably a result of rapid reaction in the combustor of this very finely divided material. The lower extent of calcination for particles collected in the cyclones is probably related to their relatively short residence times in the reaction zone due to their intermediate size.

c. Calcium Utilization. The extent of conversion of CaO to $CaSO_4$ for bed and elutriated materials was calculated from the Ca/S mole ratios for materials from several series of experiments. The Ca/S mole ratio in a solids stream was calculated from calcium and sulfur concentrations determined by wet chemical analysis.

Average values and ranges of calcium utilizations have been obtained for solids streams from the SA-, BC-, and AR-series experiments (Table 5). The major difference observed is the higher degree of utilization of calcium in the fluid-bed solids for the SA-series than for the BC- or AR-series, due most probably to the use of a smaller particle size of limestone additive in the SA series.

The Ca/S mole ratios for solids streams of Amer and Brit experiments also were calculated from the calcium and sulfur contents of the solids. In most runs, the Ca/S mole ratios in the fluidized-bed and final-filter solids were 0.9-3.4, and are close to the Ca/S mole ratios (1-3.6) of the coal and limestone feed streams (Table 1). The calcium utilizations for the primary and secondary cyclone solids were low, corresponding to Ca/S ratios of 3.3 to 10.9. Probably, the lower extent of sulfation of the solids in the cyclones was due to their shorter residence times in the combustor reaction zone. The higher calcium utilization for the final-filter solids was probably a result of their small size (evidenced by their passage through the cyclone separators) and greater reactivity.

d. Hydration of Partially Sulfated Limestone. Because samples from the cyclones and fluidized bed contain partially sulfated limestone that is highly calcined (99% or greater), the weight of a sample submitted for analysis could increase upon exposure to the atmosphere since hydration of lime (CaO) to form the hydroxide, $Ca(OH)_2$, occurs readily. An increase in the weight of a sample because of hydration of compounds in the sample could affect the value reported as the percentage of a component--sulfur, calcium, or carbon--in the sample. Therefore, experiments were performed to determine the rate and extent of hydration of partially sulfated fluidized-bed and cyclone samples by exposing samples to the atmosphere and weighing them at intervals.

From analyses of the exposed fluidized-bed samples for CaO, the hydration rate was found to be initially about 2%/hr and to drop rapidly to about 0.5%/hr. Some samples continued to gain weight beyond the point at which hydration was theoretically complete. Weight gain continued at a very slow rate, about 0.1%/hr. This additional pickup of moisture may be a result of water being absorbed on an active limestone surface. Since fluidized-bed material is exposed only briefly to the atmosphere during analysis, excessive hydration is not expected.

e. Calcium Sulfite Formation. The possibility that calcium sulfite formation and calcination are related through a common mechanism was suggested by the results of an earlier BMI coal combustion study[5] in which sulfite was found in the reacted limestone. The fraction of sulfur in the form of sulfite was related to the degree of calcination. Although there is considerable scatter in the data presented, an inverse relationship

TABLE 5. Calcium Utilizations for the SA, BC, and AR Series

	Experimental Conditions							Calcium Utilization (%)			
Expt. Series	Type of Additive	Size of Additive (μm)	Temp (°F)	Gas Velocity (ft/sec)	Ca/S[a]	Starting Bed		Primary Cyclone	Secondary Cyclone	Fluid Bed	Final Filter
SA	No. 1359	25-103	1550-1650	3.0	Varied 0-4.0	Alumina	Average	20	40	70	70
							Range	14-24	38-45	67-71	62-100
BC	BC-6, -7,-8 No. 1359 BC-9 No. 1360 BC-10 No. 1337	44-650	1480-1800	2.7-3.2	2.2-2.5	Calcined-Sulfated Lime	Average	35	25	44	84
							Range	21-47	21-29	32-54	56-100
AR-1, -2,-4	No. 1359	490	1400-1600	2.5-2.8	2.5-2.8	Calcined-Sulfated Lime	Average	25	29	41	67
							Range	21-29	26-31	40-42	56-77
AR-5	No. 1359	490	1550	~2.8	2.5-5.5	Calcined-Sulfated Lime		-	-	20-30	23
AR-6	No. 1359	1640	1550	3.5-7.4	3.8-4.2	Calcined-Sulfated Lime		13-17	27-28	15-20	45

[a] Calculated ratio of calcium in additive fed to combustor to sulfur in coal fed to combustor.

could possibly be postulated. For example, according to BMI, the molar percent of sulfur present as sulfite was in the 55-65% range at ~25% calcination, in the 10-30% range at 80% calcination, and in the 5-25% range at 95% calcination. The suggested reactions include the following:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (4)$$

$$CaO(s) + SO_2(g) \rightarrow CaSO_3(s) \qquad (5)$$

$$CaSO_3(s) + 1/2\ O_2(g) \rightarrow CaSO_4(s) \qquad (6)$$

$$4\ CaSO_3(s) \rightarrow CaS(s) + 3\ CaSO_4(s) \qquad (7)$$

The presence of calcium sulfite in the products from limestone-SO_2 reaction is being studied at Argonne. The sulfite levels of fluidized-bed samples were expected to differ from sulfite levels in samples of elutriated solids. Fluidized-bed particles have relatively long residence times and are heated to the combustion temperature (in excess of 1400°F, where $CaSO_3$ is thermodynamically unstable), and such particles would be expected to contain little sulfite. In contrast, sulfite may be detected in the elutriated solids collected in the primary and secondary cyclones, which may not have reached combustion temperatures (the calcination reaction is endothermic) because of shorter residence times in the combustor.

At ANL, elutriated material from each cyclone separator in experiments BC-2 to -5 (performed at 1600°F; see ANL/ES/CEN-1002, p. 47) was analyzed for sulfite. The particle sizes of the Tymochtee dolomite additive were 650 μm for BC-2 and -3 and <44 μm for BC-4 and -5. The extent of calcination for samples from the primary cyclone ranged from 76 to 81%, and that for the secondary cyclone was 87 to 96%.

Sulfite was not detected in solids from BC-2; however, sulfite was detected in the three other experiments up to a maximum of 0.23 wt %. A sulfite concentration of 0.23% in the cyclone samples corresponds to 4.2% of the total sulfur fed. In the BMI study,[5] 10 to 30% of the sulfur was in the form of sulfite at the same extent of calcination. It is thought that the samples in which no sulfite was detected had been heated to 1400°F or higher. The fact that sulfite was not found does not preclude it as an intermediate as suggested by Battelle.

f. Particle Size of Fluidized-Bed Material. The particle size distributions of input and output solids streams for experiments Amer-1, Amer-3, Brit-1, Brit-3, Brit-Amer, and Amer-Brit (Table 2) were determined to identify any changes in particle size distribution in the bed as a result of passage through the screw feeder, elutriation, additive feed rate, and type of starting bed. In these runs, the gas velocity was ~2.6 ft/sec.

The particle size distributions for limestone No. 1359 (used in Amer and Brit-Amer experiments) before and after it had passed through the screw feeder were measured. Passage through the screw feeder resulted in the +25 mesh fraction decreasing from 40.4 to 33.1 wt % and the -325 mesh fraction increasing from 8.2 to 11.1 wt %.

In the Amer experiments, Illinois coal was burned. It was assumed in interpreting the results of particle size analyses that the ash generated was elutriated overhead and did not accumulate to an appreciable extent in the bed.

In experiment Amer-1, the limestone feed rate was 0.53 lb/hr. The starting bed material was the final bed (partially sulfated and calcined limestone) from experiment AR-5. A major change was observed in the particle size distribution of the bed material during this 39-hr run—the percentage of +25 mesh particles increased from 13.6 to 21.5. Also, the -170 mesh particles in the starting bed apparently were removed by elutriation early in the experiment, and the percentage of -80 +170 mesh particles dropped from 7.2 to 2.1.

In experiment Amer-3, the limestone feed rate was three times as great as in Amer-1, about 1.6 lb/hr, and the original bed material was the final bed from Amer-1. At this higher feed rate, the particle size distribution in the bed changed significantly. The percentage of +25 mesh particles in the bed after 6 hr of operation was 40.6 wt %, as compared with 21.5 wt % after 39 hr of Amer-1. The percentage of +25 mesh particles in the final fluidized-bed sample for this 21-hr experiment also was high, 41.4%. Bed samples taken during Amer-3 contained no -170 mesh particles, which apparently had elutriated. When the particle-size distribution for limestone additive was recalculated with the -170 mesh fraction omitted, the calculated distribution was similar to the particle size distribution found in Amer-3 bed material after 21 hr.

To determine any changes in particle size distribution during Brit-series experiments, particle size distributions of input solids streams (Welbeck coal and CRE limestone) and fluidized-bed samples for experiment Brit-1 were measured, as well as those for coal ash (the starting bed). The limestone addition rate was only 0.4 lb/hr, and the coal ash accumulation in the bed (assuming no elutriation) may have been several times the limestone addition rate. The data show that the particle size distribution of the fluidized bed at the end of the experiment differed little from the size distribution of the original coal ash.

During experiment Brit-3, with a limestone feed rate of 0.23 lb/hr, the particle size distribution of the bed remained relatively constant. The +25 mesh fraction, which constituted 27% of the bed material at the end of Brit-1, had decreased to 19% at the end of experiment Brit-3.

Particle-size distributions were determined for the Brit-Amer experiment, in which British coal and American limestone No. 1359 were fed. In this short duration experiment (4 hr) with a low limestone feed rate (0.38 lb/hr), particle size distribution in the bed did not change significantly. In the 8-hr Amer-Brit experiment, which utilized American coal and British limestone, the particle size distribution did not differ significantly from those for the Brit-Amer and Brit experiments. In general the particle size distribution of the bed particles does not change significantly during an experiment.

g. Decrepitation of Additive Particles. Decrepitation and attrition of several additives during coal combustion experiments has been estimated by comparing the calcium content of elutriated material with the calcium content of fines in the bed. (The starting fluidized bed also contained calcium.) In most experiments a gas velocity of ~2.6 ft/sec was used; at this velocity, it is expected that all of the flyash and additive particles having diameters of <177 µm will be elutriated from the fluidized bed and that their calcium content would be found in the elutriated material. Because the particulate matter that is elutriated during the combustion of coal in a fluidized bed is a mixture of solids of different origins and compositions, the fraction of additive carried over can only be estimated.

The expected elutriation of additive for Amer-, BC-, AR-, and Brit-series experiments was calculated and compared with the actual elutriation determined from calcium material balances. (An allowance was made for the calcium content of the flyash, which was also elutriated.) The difference between actual and expected elutriation was the estimated decrepitation of large additive particles.

It is estimated that decrepitation of No. 1359 limestone was ~8%. No decrepitation of British limestone was evident. Decrepitation of limestone No. 1360 and dolomite No. 1337 particles was more severe—40 and 85%, respectively. These results indicate that limestone No. 1359 and British limestone are desirable materials for use in a full-scale fluidized-bed combustor if the additive is to be regenerated and recycled. The higher decrepitation rates for No. 1360 and 1337 additives may make these materials less promising for regeneration and recycle.

h. Bulk and Tapped Densities of Solids from the Bed, Cyclones, and Final Filter. Bulk and tapped densities of fluidized-bed material and of solids collected in the cyclones and final filter in Amer and Brit experiments were determined. The bulk densities of the cyclone and final-filter solids ranged from 0.15 to 0.77 g/cc, and the tapped densities from 0.23 to 1.1 g/cc. These low densities were due most probably to the nature of the solids, which consist of coal ash and/or limestone fines. The bulk and tapped densities of the fluidized-bed solids were very similar to those of the precursor solids. In the Amer experiments, the precursors were limestone No. 1359 and possibly small amounts of Illinois coal ash; in the Brit experiments, the precursors were Welbeck coal ash and small amounts of British limestone.

4. Material Balances

Material balances for sulfur, carbon, and calcium in several series of runs are tabulated below.

	Sulfur	Carbon	Calcium	Magnesium
Amer-1,-3,-4	113%	97%	92%	
Brit-1 to -3, Amer-Brit, Brit-Amer	98%	114%	92%	
BC-6 to -10	81%	97%	87%	
BC-10 (dolomite additive)				99%
AR-1,-2,-4,-5,-6	82%	97%	82%	

The experimental conditions for these experiments are given in Table 1 of this report and in ANL/ES/CEN-1002, Table 8. The procedure for calculating material balances in these ANL runs is presented in Appendix C, along with details on the weights of sulfur, carbon, and calcium in each material entering and leaving the combustor.

5. Exploratory Two-Stage Combustion Runs

Four exploratory runs (Amer-7A to -7D) using two-stage combustion (see Section III.C. for procedure) were the first two-stage runs made at ANL to determine the effect of this mode of combustion on SO_2 and NO_x concentrations in the flue gas. In two-stage combustion, a substoichiometric volume of combustion air is fed at the base of the fluidized bed, and a second volume of air is fed into the space above the bed to burn CO and hydrocarbons in the gas leaving the fluidized bed. The hot gases from the second stage would be directed to a gas turbine.

In each part of Amer-7, the secondary air was injected 6 in. above the fluidized bed. In Amer-7A and -7B, the secondary air was injected downward (toward the bed and countercurrently to the fluidizing-gas flow); in Amer-7C and -7D, air was injected upward (away from the bed and cocurrently with the fluidizing-gas flow). These runs were made with Illinois coal and limestone No. 1359 additive at fluidized-bed temperatures of 1450 and 1550°F. The Ca/S mole ratio was ~3, and the fluidizing-gas velocity was ~1.9 ft/sec. The starting bed was partially sulfated and calcined limestone No. 1359. Operating conditions and results are given in Table 6.

a. Sulfur Retention. During Amer-7A, the fluidized-bed temperature was maintained at 1550°F. The concentrations of SO_2 in the flue gas at steady-state combustion was ~3000 ppm. The temperature 16 in. above the secondary air inlet point (probably in the CO combustion zone) was only ~1020°F, showing that the gas cools rapidly after leaving the bed (which was at ~1550°F).

When secondary air injection was stopped in Amer-7A, the concentration of SO_2 in the flue gas decreased from 3000 ppm to about 800 ppm. Upon the resumption of air injection, the SO_2 concentration returned to the original value of 3000 ppm. This suggests that secondary air may have been reacting with a compound in the bed to form SO_2.

In Amer-7B, operating conditions were maintained essentially the same as in Amer-7A except that a lower fluidized-bed temperature, 1450°F, was used. At steady-state combustion, the SO_2 concentration in the flue gas was 1100 ppm. Interruption of secondary gas flow caused the SO_2 concentration to decrease to 400 ppm, and resumption of air injection returned the SO_2 concentration to 1100 ppm. The different SO_2 levels at 1450 and 1550°F indicate that SO_2 emission was affected by combustion temperature.

Secondary air was injected cocurrently into the fluidizing gas during Amer-7C; all other operating conditions were essentially the same as in Amer-7A. Concentrations of SO_2 in the flue gas after steady state was attained were 3000 and 500 ppm, respectively, for Amer-7A and -7C.

TABLE 6. Effect of Cocurrent and Countercurrent Flow of Secondary Air in Two-Stage Combustion

Equipment: ANL 6-in.-dia fluidized-bed combustor

Coal: Illinois (3.7 wt % S; -14 mesh)

Additive: Limestone No. 1359, as received

Starting Bed: Partially calcined and sulfated limestone No. 1359

			Feed Rates					Flue Gas Concentrations					
Expt. Amer-	Fluidized-Bed Temperature (°F)	Total Run Time (hr)	Coal (lb/hr)	Additive (lb/hr)	Ca/S Mole Ratio	Fluidizing-Air Velocity (ft/sec)	Secondary Air Injection Rate (% of Total Air Feed)	O_2 (vol %)	CO_2 (vol %)	CO (ppm)	NO (ppm)	SO_2 (ppm)	Sulfur Retention (%)
7A[a]	1550	6.5	5.0	1.7	2.9	1.9	20	0.9	18.5	6000	100	3000	43
7B[a]	1450	6.5	5.1	1.8	3.0	1.8	20	1.0	17.2	6400	100	1100	80
7C[b]	1550	7.0	5.2	1.8	3.0	1.8	16	1.0	15.9	7800	70	500	91
7D[b,c]	1550	11.0	5.2	1.8	3.0	2.1	13	1.0	17.5	6500	70	1000	81

[a] Direction of secondary air flow was down, toward the fluidized bed.

[b] Direction of secondary air flow was up, away from the fluidized bed.

[c] Upper section of combustor (where the secondary air was reacting with CO and hydrocarbons) was insulated.

The higher SO_2 concentration levels during Amer-7A and -7B, in comparison to SO_2 levels in Amer-7C, and the decrease in SO_2 levels upon interruption of air injection from the probe in Amer-7A and -7B indicate that possibly the following reactions occur. In the lower part of the combustor, where too little oxygen is available for complete combustion, one or both of the following reactions are postulated:

$$CaSO_4 + 4\ CO \rightleftarrows CaS + 4\ CO_2 \qquad (8)$$

$$CaO + H_2S \rightarrow CaS + H_2O \qquad (9)$$

When air is injected countercurrently into the off-gas from the fluidized bed, a portion of the bed solids may be exposed to the air jet and the following reaction may occur:

$$CaS + 1\ 1/2\ O_2 \rightleftarrows CaO + SO_2 \qquad (10)$$

Sulfide has been found in samples removed from the bed.

The sulfur retention corresponding to the 500 ppm SO_2 concentration in the flue gas in Amer-7C is 91% (Table 6). This may be compared with the sulfur retention of 80% obtained in one-stage combustion run Amer-8B. In Amer-8B, the coal, limestone, and bed temperatures were the same as in Amer-7C, but the Ca/S ratio was $\sim$4 rather than 3.0 used in Amer-7C. It would be expected that SO_2 removal would be less than 80% in Amer-7C since this run was performed at a Ca/S ratio of 3.0 and with other Amer-8B operating conditions.

In run Amer-7D, an attempt was made to increase the gas temperature above the fluid bed by insulating the top section of the combustor. Thereby, the amount of CO and hydrocarbons combusted might be increased. Temperature in the second stage, which was 980°F in Amer-7C, was 1275°F in run Amer-7D. The SO_2 concentration in the flue gas in run Amer-7D reached 1000 ppm, compared with 500 ppm observed in run Amer-7C (which was made at the same conditions but with the second stage uninsulated). To account for the increased SO_2 level at the higher second-stage temperature, it is suggested that CaS in the solids being elutriated from the fluidized bed reacted with oxygen, releasing SO_2 (reaction 10) and that the reaction rate was greater at the higher temperature. This preliminary result also suggests that provision should be made to remove most of the solids from the flue gas prior to second-stage combustion.

b. Emission of NO. The concentrations of NO in the flue gas in these two-stage runs ranged from 70 ppm during Amer-7C to 100 ppm during Amer-7A and -7B. In contrast, NO levels in one-stage combustion have ranged from 180 to 500 ppm. The 70 ppm level corresponds approximately to the equilibrium NO concentration expected at this temperature and oxygen concentration. The low NO level experienced in two-stage combustion indicates that with this mode of operation, nitrogen is not oxidized to NO during the combustion process because of the high CO concentrations present in the bed.

c. CO Concentration in the Flue Gas. The concentrations of CO in the flue gas were 6000, 6400, 7800, and 6500 ppm, respectively, for Amer-7A, -7B, -7C, and -7D. During Amer-7A and -7B, interruption of secondary air injection through the probe resulted in higher levels of CO concentrations in the flue gas. Since oxygen-deficient conditions in the fluidized bed produced high concentrations of CO and the low temperatures prevalent at the downstream side of the fluidized bed did not favor the combustion of CO to CO_2, only about one-fourth of the CO reacted. It was also observed that when the temperature of an upper section of the combustor was increased from 977°F (525°C) in Amer-7C to 1275°F (690°C) in Amer-7D, the CO concentration decreased (see Table 6), indicating that the CO levels in the flue gas might be further lowered by increasing the temperature of the off-gas stream.

III. MECHANISM OF THE LIME SULFATION REACTION

A. Introduction

The mechanism by which the reaction between lime and SO_2 occurs to form $CaSO_4$ has been speculated upon and investigated by various groups[6-10] outside this laboratory. In general, the two main hypotheses for the reaction can be called the continuous reaction and the shell-formation models. In the continuous model, the reaction is considered to occur more or less uniformly throughout the lime particle, with the sulfating gas passing into the interior of the particle through pores. In the shell model, the initial reaction occurs on the surface of the particle; the continuing reaction proceeds by passage of the sulfating gas through this initial sulfate layer, and the shell thickness increases with time. The controlling factors in these two reaction models would be gas diffusion through the pore structure in one case and through the $CaSO_4$ shell in the other.

Experimental work reported by Borgwardt[6] of OAP supports the continuous-reaction model, while work reported by Hatfield and Kim[7] at the TVA Muscle Shoals site supports the shell-reaction model. Both modes of reaction were supported by workers at Battelle Memorial Institute (BMI)[8]—the continuous model for an oxygen-deficient reaction condition and the shell model for the oxygen-sufficient reaction condition. In a study employing X-ray diffraction and electron microscopy, McClellan and coworkers[9] came to the conclusion that the sulfation reaction follows the shell model. Of interest in the results reported by McClellan and coworkers is that $CaSO_4$ crystallite size was dependent on whether the calcination and sulfation reactions occurred simultaneously or consecutively. The crystallite size was smaller when the reactions occurred consecutively.

The reaction for sulfation under oxygen-rich conditions can be written as follows,

$$CaO + SO_2 + 1/2\ O_2 = CaSO_4 \qquad (11)$$

which can, in turn, be represented by the following pairs of reactions

$$\text{either}\quad CaO + SO_2 = CaSO_3 \qquad (12)$$

$$CaSO_3 + 1/2\ O_2 = CaSO_4 \qquad (13)$$

$$\text{or}\quad SO_2 + 1/2\ O_2 = SO_3 \qquad (14)$$

$$CaO + SO_3 = CaSO_4 \qquad (15)$$

It has not been shown which reaction route prevails at the nominal fluidized-bed temperature of about 1600°F. The presence of neither $CaSO_3$ nor SO_3 is favored at this temperature; the SO_2 dissociation pressure from the equilibrium for equation 12 is about 0.04 atm, while the SO_3 partial pressure for equation 14 is about 3×10^{-5} atm at equilibrium concentrations of SO_2 and O_2 of 0.0004 and 0.03 atm, respectively, which would be the nominal concentration of these effluents from a fluidized-bed combustor. Although these equilibrium data favor the reaction path employing the reaction of

SO_2 with lime, no kinetic data are available and the reaction path cannot be stipulated at this time.

In work being performed in England on fluidized-bed gasification, the reaction route through SO_3 is advocated.[10] Workers at BMI[11] have shown, in experiments simulating limestone injection into flue gas for SO_2 pickup, that the short-time reaction produces mainly sulfite, while longer-term reactions produce sulfate.

It must be kept in mind that most of the studies of the limestone-SO_2 reaction to date have been directed at conditions existing for limestone injection into conventional pulverized-coal furnaces. This type of operation involves shorter reaction times and higher reaction temperatures than in a fluid-bed combustor where the lime particles would be retained for extended periods of time. Therefore, data from the above-described investigations can only be used to guide the fluid-bed combustion program.

In the ANL fluidized-bed program, the mechanism of the lime-SO_2 reaction has been a continuing area of interest. Early in the program, it was evident that knowledge of the mechanism of the reaction would be important in devising the most efficient reaction conditions for reducing SO_2 emission. Ample evidence exists from the ANL work that the mechanism of sulfur oxide suppression in the fluidized-bed combustor is much more complex than simple consecutive reactions involving CaO, SO_2, and O_2. Many anomalous results have been observed that cannot be explained by the reaction pair. eq. 12 and 13, or the alternative reaction pair, eq. 14 and 15. It is reasonable to suppose that the above reactions do occur in the combustor, but that these reactions alone are not sufficient to account for all of the observed results. Some of the evidence that supports a more complex mechanism is the following:

1. When natural gas is burned in a partially sulfated bed of lime (without fresh limestone addition), SO_2 is released from the bed at temperatures as low as 1650°F; yet in the absence of combustion, decomposition of $CaSO_4$ is known to occur only at much higher temperatures (>2000°F).

2. The optimum temperature range for sulfur retention in the ANL combustor has been observed to be 1450 to 1550°F. This temperature range is appreciably lower than the optimum for SO_2 removal from flue gases outside the combustor (>1600°F). In the fluidized-bed combustor, sulfur retention efficiency rapidly decreases at temperatures above 1600°F.

3. In the fluidized-bed combustor, the optimum temperature for sulfur retention possibly varies with the Ca/S ratio, being lower at high ratios of Ca/S. This is contrary to the expectation that the CaO-SO_2-O_2 reaction should exhibit a fixed optimum temperature for a particular type of lime.

4. Recycle of flyash containing partially sulfated lime to the fluidized-bed combustor at ANL does not increase SO_2 removal to an observable extent; yet this same flyash material is found to have considerable capacity to react with SO_2 when a sample in a boat is exposed to dilute SO_2-air mixtures in a furnace.

5. When less-than-stoichiometric air is fed to the bottom of the combustor and a stream of secondary air is directed toward the top of the bed, sulfur retention by the lime bed is very poor; yet when the secondary air stream is directed cocurrently with the off-gas and does not contact bed material, sulfur retention is good.

The above observations suggest that the combustion process itself influences sulfur oxide reaction with lime. During fluidized-bed combustion, the sulfur appears to have an exceptional mobility for penetration into lime particles. The observation that SO_2 can be released from bed material at rather low temperatures (1650°F) during combustion of natural gas suggests that chemical reduction of $CaSO_4$ occurs despite the introduction of excess air to the bottom of the bed. The need to employ a relatively low temperature (1450-1550°F) for optimum sulfur retention by the lime bed may be influenced by the rate of the reduction reaction.

1. Mechanism - Macro Effects

Because not all needed information is on hand, our current concept of the mechanism is necessarily speculative. Nevertheless, a summary of our current thoughts about the mechanism might help illustrate its complexity.

It is necessary, first, to consider the flow behavior of gases in the fluidized bed. When air enters the bed at the gas distributor, a portion of the gas flows through the bed in intimate contact with the solids. This mixture of gas and solids is called the emulsion phase. The remaining portion of the air flows through the bed in the form of gas bubbles. As the bubbles rise through the bed, gas from the bubbles continually circulates into the emulsion phase and back into the bubbles. The gas in the bubble phase reacts only as it circulates through the emulsion phase. On the basis of combustion efficiency data for the fluid-bed combustor, it is known that circulation of air from the bubbles to the emulsion phase is essentially complete by the time the bubbles leave the bed. Nevertheless, it is reasonable to assume that in the lower portion of the fluidized bed, not all of the air from the bubble phase has circulated into the emulsion phase and that the emulsion phase contains a deficiency of air. Thus the emulsion phase in the lower part of the bed would contain a reducing atmosphere, and the emulsion phase in the upper part of the bed would contain an oxidizing atmosphere.

The behavior of sulfur under the above conditions can be illustrated by an extreme example from experimental work. In one part of a two-stage coal combustion experiment (Amer-7A), the reducing condition in the bed was accentuated by feeding less-than-stoichiometric air at the bottom of the bed. The sulfur concentration in the flue gas was 800 ppm. In another part of the same experiment, additional secondary air was introduced through a tube in such a way that the air impinged on the top of the bed and the sulfur concentration in the flue gas increased to 3000 ppm. These results suggest that sulfur was accepted by the lime in the lower part of the bed, forming CaS, but that reaction of the sulfite with excess air in the upper part of the bed released SO_2. Of course, in a run made under typical single-stage combustion conditions, extreme effects such as those in this example would not be encountered.

It is well known that $CaSO_4$ can be reduced rapidly to CaS by reducing gases such as CO or hydrogen at temperatures of about 1750°F. At lower temperatures, the rate decreases, and not much is known quantitatively about the kinetics at lower temperatures. The reaction of CaS with air to produce CaO and SO_2 is also well known, but again little is known about the kinetics at the temperatures commonly used in the fluid-bed combustor.

It is reasonable to assume that at some fluidized-bed temperatures, a small portion of the $CaSO_4$ in the bed can be reconverted to CaO and SO_2 by a mechanism involving circulation of the particles into localized reducing atmospheres resulting from fuel combustion. This was borne out in an experiment in which evolution of SO_2 was observed during combustion of natural gas in a partially sulfated bed at 1650°F. If oxidation of small amounts of CaS is a part of the mechanism, some SO_2 may be generated near the top of the bed, limiting the overall sulfur removal.

It appears that the reaction in which $CaSO_4$ is formed from lime and SO_2 is continually being reversed by exposure of the $CaSO_4$ to localized reducing conditions in the lower portion of the bed. The importance of the reverse reaction would depend upon the conditions in the combustion bed; lower temperatures would minimize the rate of the reverse reaction, high concentrations of reductants would tend to promote the reaction. Thus, the net SO_2 retention could be influenced by combustion conditions and by the distribution of fuel (or the distribution of reducing agents) in the bed. In a large combustor, for example, the number of coal feed points might influence SO_2 removal. Since different coals burn at different rates, the local concentrations of gaseous reductants in the bed may vary for different types of coal. Thus, the type of fuel burned may influence sulfur removal, and the optimum combustion temperature may vary slightly for different types of fuel. A number of other factors could be important; for example, in a large combustor with a deep bed that is heavily baffled by steam tubes, the rate of solids circulation would be reduced, thus decreasing the reverse reaction. Such factors could account for the variability of results achieved in various types and sizes of combustors using various types of coal.

2. Mechanism - Micro Effects

If the circulating bed particles are continually cycling into and out of a reducing atmosphere and SO_2 can thereby be regenerated from the $CaSO_4$, this would have an effect on the sulfation of individual additive particles. When a fresh lime (or limestone) particle is fed to the bed, reaction with SO_2 occurs rapidly and $CaSO_4$ forms, mostly on the outer surfaces and in the pores of the particle. A condition is soon reached wherein the probability that an SO_2 molecule will be released from the particle by the reduction mechanism is almost as great as the probability that an SO_2 molecule will be accepted from the bulk gas phase. The particle would then appear to have a low reactivity for SO_2, although it would still have a considerable capacity for accepting SO_2 at a low rate.

The average residence time of a particle in the fluidized bed is several hours. During this long residence period, the particle would be subjected to many cycles of alternate reducing and oxidizing conditions.

Any SO_2 released by the reduction mechanism would have an opportunity either to penetrate deeper into the particle or to escape into the gas phase. Ultimately, a condition would be reached wherein the sulfur would be uniformly distributed within the particle at a concentration determined by a pseudoequilibrium set up by the sulfur acceptance and rejection cycle. This sulfur concentration would be appreciably less than that represented by total conversion of $CaSO_4$ since at this level of sulfation, any additional pickup of SO_2 would be balanced by release of SO_2 and the sulfur level would remain constant.

The above-conjectured mechanism would limit total sulfur pickup by the lime particles. On the other hand, the sulfur would have a greater mobility for penetration into particles, and there would be no sulfate shells (which would seriously reduce the reactivity and capacity). As mentioned previously, preliminary experimental data indicate that the net effect is that fluidized lime beds in which combustion is occurring have a greater reactivity and capacity for SO_2 removal than do similar beds in which combustion is not occurring.

Let us now consider the fine lime particles contained in recycled flyash. These particles, which are only lightly converted to sulfate, have considerable capacity for accepting additional SO_2, as is observed when they are exposed to SO_2-containing gases outside the combustor. Yet when the elutriated material is recycled to the combustor, the additional lime has little apparent effect on SO_2 retention. This could be explained by assuming that the outer sulfate-bearing portion of the particles is already in sulfur-equilibrium with the fluidized-bed combustion medium. Because these fine particles have a very short residence time in the fluidized bed, further sulfur penetration into the particles is insignificant. Thus, the recycled particles pass through the combustor bed with little apparent reaction.

Next considered is feeding (to a coarse-particle bed of partially sulfated lime) of coal and limestone at rates corresponding to very high ratios of lime to sulfur. As the Ca/S ratio is increased, the average residence time of the additive particles decreases proportionately. At high Ca/S ratios, the probability that an SO_2 molecule will be picked up near the outer surface of a relatively fresh particle rather than penetrating into an aged particle increases. Thus, at high Ca/S ratios, a sulfur gradient within a particle is more likely. Under these circumstances, the relative effect of the "reverse" reaction (reduction of $CaSO_4$) becomes greater, and the temperature for optimum SO_2 removal is slightly lower. This hypothesis conforms to the experimental evidence that the optimum combustion temperature is lower at a Ca/S ratio of four (1450°F) than at a Ca/S ratio of two (1550°F).

B. Experimental

The mechanism of the sulfation reaction has been investigated by two approaches: (1) microprobe examination of sulfated lime particles to determine the sulfur distribution and (2) laboratory-scale reduction of sulfated limestone under moderate temperature conditions. An objective of the latter experiments was to evaluate the hypothesis that the sulfation reaction proceeds via alternate sulfation and reduction by studying the evolution of SO_2 from sulfated limestone. Microprobe examination would reveal differences in the distributions of sulfur in lime particles that in turn might indicate how the mechanism of sulfation during coal combustion differs from the mechanism when limestone is exposed to a SO_2-air mixture during natural gas combustion.

A Model EMX-SM electron microprobe manufactured by Applied Research Laboratory was used to examine sulfated lime particles. The electron probe analyzer offers nondestructive, in situ elemental analysis of areas as small as one square micrometer. It can quantitatively determine all elements having atomic numbers higher than that of sodium in samples as small as a few cubic micrometers in volume, or on surfaces as small as 1 μm in diameter. Accuracy is 1-2%. The probe uses the sample as a target for a magnetically focused beam of highly accelerated electrons. Upon striking the sample, the electrons excite the emission of X-rays, whose wavelengths characterize the elements present and whose intensities yield concentrations. When the probe is adapted for scanning instead of point analysis, it provides a clear map of element distribution over the sample surface. The equipment and instrument components of the bench-scale fluidized-bed combustor, in which the solids examined with the microprobe were generated, are described in detail in Section III.B of this report. The partially sulfated particles sampled for electron probe examination were cold-mounted in Polylite, polished through 1-μm diamond paste, then either carbon- or gold-coated by vacuum sputtering. Microphotographs were then made of selected particles or areas of the mounts to guide the microprobe work.

The equipment (Fig. 10) for laboratory-scale study of the evolution of SO_2 from sulfated lime in a reducing atmosphere was a modified portion of the laboratory-scale apparatus constructed for high-pressure chemical reaction studies. It comprised an electrically heated 2-in.-dia stainless steel vertical fixed-bed reactor, associated manifolding for supplying and mixing pure gases from cylinders, and provisions for water saturation of the feed gas stream at the inlet to the reactor. The off-gas from the reactor was dried and filtered prior to continuous analysis by the analytical system described in ANL/ES/CEN-1002, pp. 21-22.

1. Microprobe Studies

a. Elutriated Particles. Samples of material elutriated to the primary cyclone in two runs were examined; one sample was taken at the end of a coal combustion experiment and the other at the end of a natural gas combustion experiment. Fresh limestone No. 1359 additive employed in these experiments had an average particle size of 25 μm and contained 97% CaO and 1.1% MgO on a calcined basis. In both experiments, the starting fluid-bed material was refractory alumina.

Electron probe scanning traces (not shown) for cross sections of four typical elutriated particles from each experiment showed that particle composition apparently is related to the type of fuel combusted. With coal as the fuel, sulfur concentration is usually lower at increasing distance from the surface of the particle; on the other hand, sulfur concentrations in particles collected during the combustion of natural gas appear to be more uniform over a range of distances from the particle surface. Only one trace out of four displays the calcium and sulfur concentrations expected for

$CaSO_4$. Traces for some particles appear to indicate that their composition was $CaCO_3$, suggesting that these fine limestone particles were not calcined when passing through the bed.

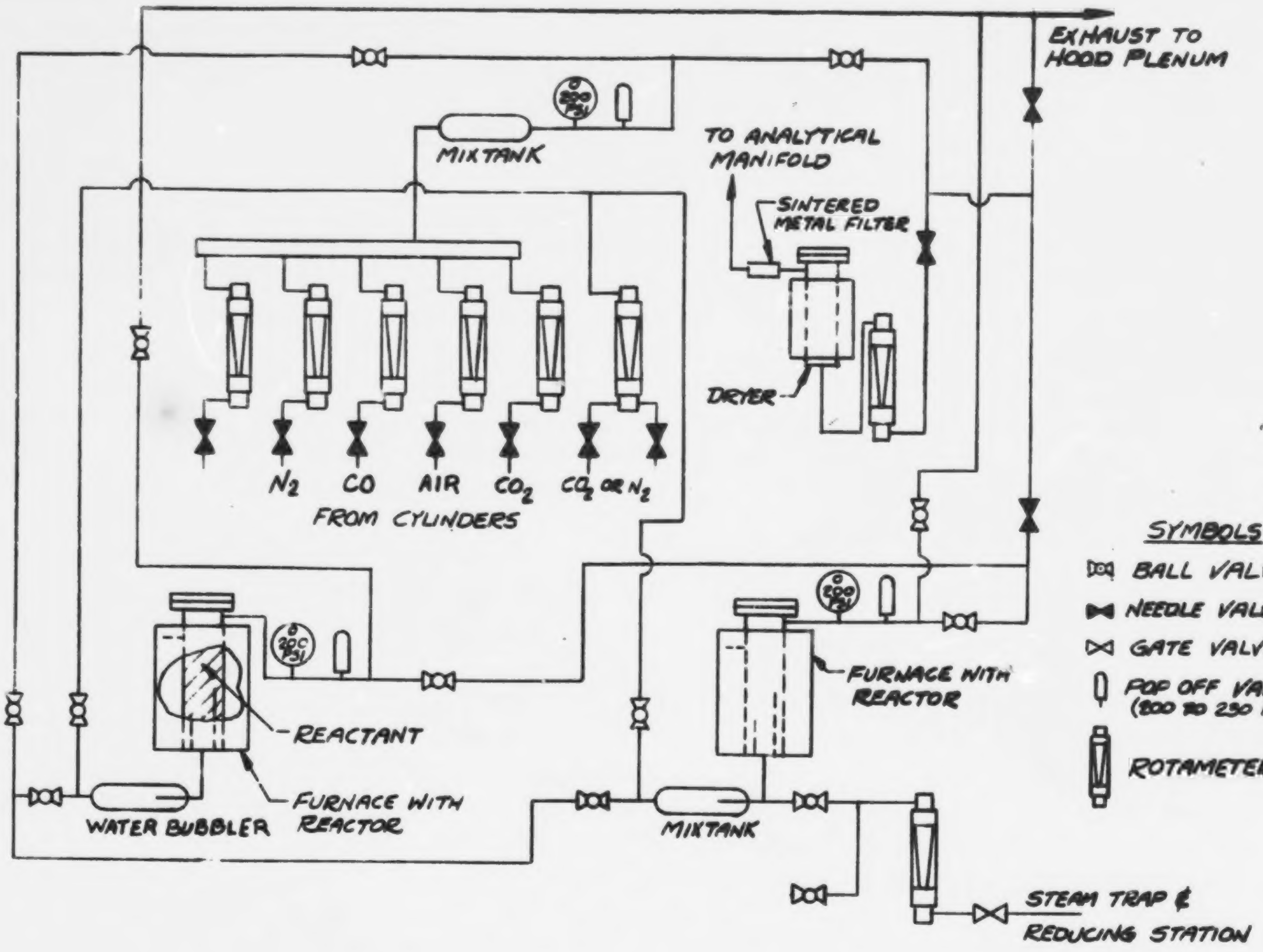

EXHAUST TO HOOD PLENUM
MIXTANK
0 200 PSI
TO ANALYTICAL MANIFOLD
SINTERED METAL FILTER
DRYER
N2
CO
AIR
CO2
CO2 OR N2
FROM CYLINDERS
SYMBOLS
BALL VALVE
NEEDLE VALVE
GATE VALVE
POP OFF VALVE (200 TO 250 PSI)
ROTAMETER
0 200 PSI
FURNACE WITH REACTOR
0 200 PSI
REACTANT
FURNACE WITH REACTOR
WATER BUBBLER
MIXTANK
STEAM TRAP & REDUCING STATION

Fig. 10. Laboratory-Scale Reactors and Associated Equipment

b. Fluid-Bed Particles. One set of electron probe analyses was performed on fluid-bed samples from coal combustion experiments BC-6, AR-1, and AR-2, in which the starting fluid-bed material was partially calcined and sulfated limestone or dolomite. (This dolomite contains 57% CaO and 42.2% MgO in the calcined state.) Sulfur, calcium, and magnesium levels over cross sections of particles of limestone No. 1359 (BC-6 and AR-2) and dolomite No. 1337 (AR-1) were measured.

Since experiments BC-6 and AR-1 were both performed under ordinary oxidizing conditions (~3 vol % oxygen in the off-gas), the distribution of sulfur across a cross section of a particle was expected to conform to that for a shell diffusion reaction mechanism model, i.e., a high sulfur concentration at the edges and a drastically lower concentration at the center of the particle. The basis for this expectation was work reported by Battelle Memorial Institute,[8] in which microprobe analysis showed a shell structure when reaction occurred under oxidizing conditions, but a uniform sulfur distribution in the particle when reaction occurred under

The sulfur traces for experiments BC-6 and AR-1 indicate that the sulfur was distributed almost uniformly over the cross sections of the 300- to 400-μm-dia particles. The average sulfur concentrations in the limestone and limestone-dolomite beds from which these particles were taken were 7.2 and 9.5%, respectively. The sulfur content for a completely sulfated limestone is calculated to be 23.5% and that for a completely sulfated dolomite 18.2%.

Scans were also performed for bed particles from coal combustion experiment AR-2 (Table 1). Part of this run was performed under relatively mild oxidizing conditions with only ∿1 vol % oxygen in the flue gas. Examples were found of both the shell model and the uniform concentration model for SO_2 reaction with limestone. Either model (the shell model or continuous penetration model) or both could and in fact appear to be involved.

At the time particle samples were taken, the fluid bed had been used for a total of about 70 hr in seven experiments (BC-6 to -10, AR-1, AR-2) and fresh limestone and dolomite had been added during these experiments. Because any one particle could have been in the bed for a long time before samples were taken, individual particle histories could not be determined. Moreover, the sulfur concentration profile for a particle having a total possible bed residence time of 11 hr is similar to that for another particle having a total possible bed residence time of 70 hr. This suggests that a long residence time in the fluid bed is not an important factor in determining the extent or shape of the sulfur concentration profile.

c. Limestone Bed Particles from Control Experiments. To eliminate the uncertainty about the reaction history of individual limestone particles, two control experiments (Table 7) were performed in the bench-scale combustor, each with a starting bed of fresh limestone and with no additive fed during the experiment. In one experiment (PB-3), the limestone No. 1359 was sulfated by SO_2 generated by the combustion of coal. In the second experiment (PB-7), the bed was electrically heated to reaction temperature, then the limestone No. 1359 was sulfated by SO_2 in a mixture with air in the absence of combustion but with heat supplied by electric heating units. Bed samples were taken frequently during the experiments.

(1) Coal Combustion Experiment PB-3. At the start of experiment PB-3, SO_2 concentration in the flue gas increased with time as the lime bed was sulfated, as expected. The SO_2 concentration finally reached a level near that predicted for the absence of absorption of SO_2 by the lime bed. Samples taken during the course of this experiment were examined with the microprobe. Seven typical sulfur traces from the microprobe analysis are shown in Fig. 11. A photomicrograph of the particle examined in scan 1 (Fig. 11) is shown in Fig. 12. Sulfur distributions shown in scans 1, 2, 4, and 6 of Fig. 11 support the idea that sulfation proceeds throughout the body of the particle. However, scans 3, 5, and 7 show sulfur concentrated in shells on the particles. The latter particles might be intermediates in the sulfation cycle, representing the condition in which sulfation is proceeding inward with time. In bed samples taken more than 2 hr after the start of a run, approximately half of the particles examined showed uniform sulfur distribution and the other half showed shells

of sulfate. The presence of both uniformly sulfated particles and particles having shells of sulfate indicates that sulfation proceeds by diffusion through a layer of sulfate.

TABLE 7. Operating Conditions for Experiments PB-3 and PB-7 in Bench-Scale Combustor

Starting Bed: Fresh Limestone No. 1359

Fluidized-Bed Temperature: 1500°F

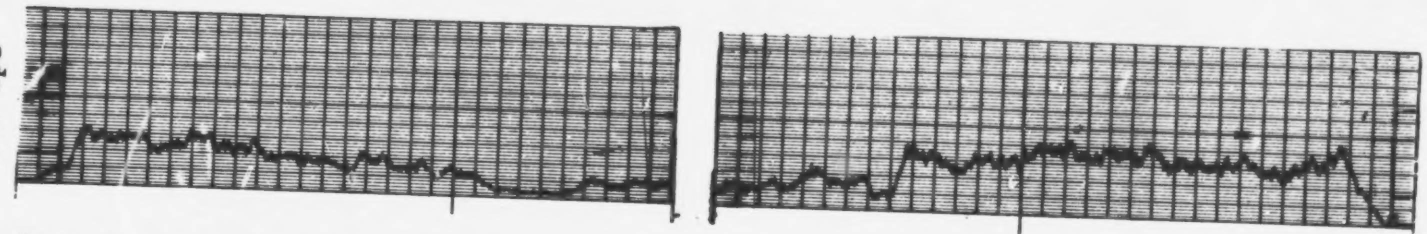
Gas Velocity: ∿2.7 ft/sec

	PB-3	PB-7
Elapsed time, hr	34	8
Source of SO_2	Combustion of -14 mesh Illinois coal	Feed of 0.6 vol % SO_2 in air, equivalent to combustion of 6.4 lb/hr coal
Coal combustion rate, lb/hr	4.5	-
Oxygen concentration (dry basis) in the flue gas, vol %	2.3	3.0

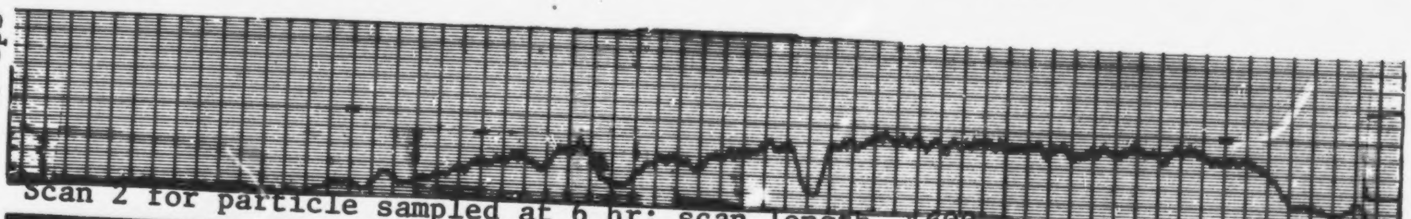
It should be noted that the maximum sulfur concentration level at any point in any of the particles examined corresponds to a count rate of about 500 cps, which is estimated to represent about 50% conversion. This maximum sulfur level is reached at the outer surfaces of the particles within 6 hr residence time. Thereafter, the sulfur level at the outer surfaces of the particles remains constant, and all additional sulfation occurs within the particles. This is also suggested by the observation that SO_2 concentration in the flue gas increases rapidly after about 6 hr.

The percentage conversion to $CaSO_4$ during the course of experiment PB-3 (Table 8) was determined by chemical analyses of bed samples. These data show that ∿30% of the lime was converted to sulfate in 14 hr and that the extent of lime sulfation essentially stayed at that level for the remainder of the experiment.

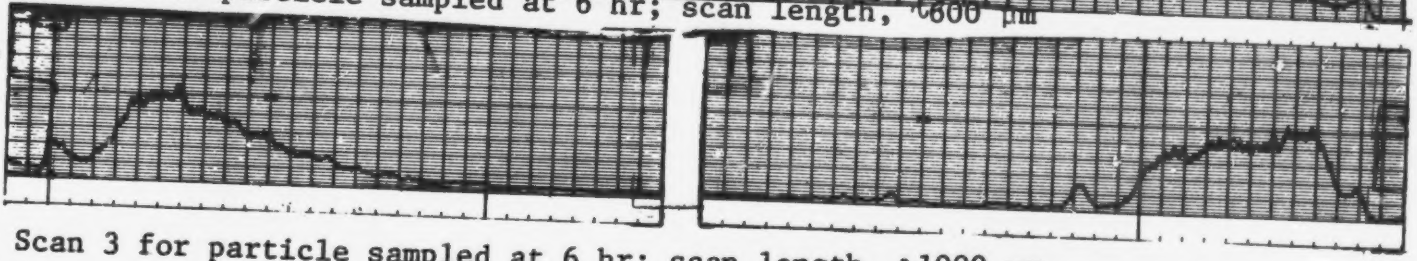
(2) Noncombustion Experiment PB-7. The SO_2 concentrations in the effluent during experiment PB-7 (in which the gas phase fed was a mixture of about 0.6 vol % SO_2 in air) were very low during the first half-hour, increased rapidly during the next hour, and increased at a moderate rate during the following 6 1/2 hr. The sulfation rate decreased much more rapidly in experiment PB-7 than in PB-3.



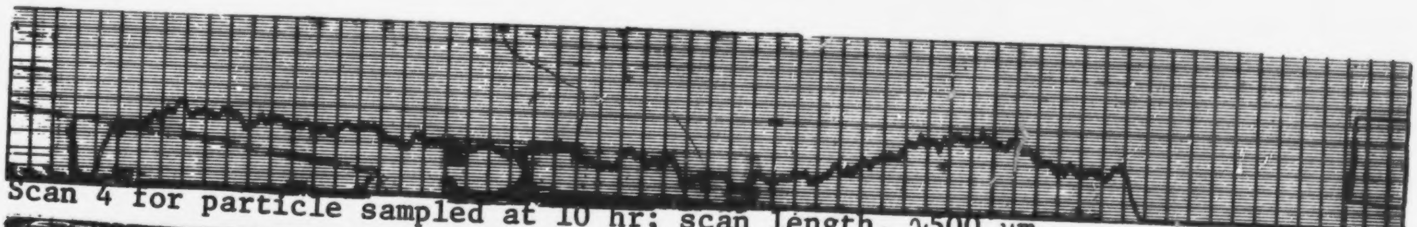
Scan 1 for particle sampled at 2 hr; scan length, ~1100 μm



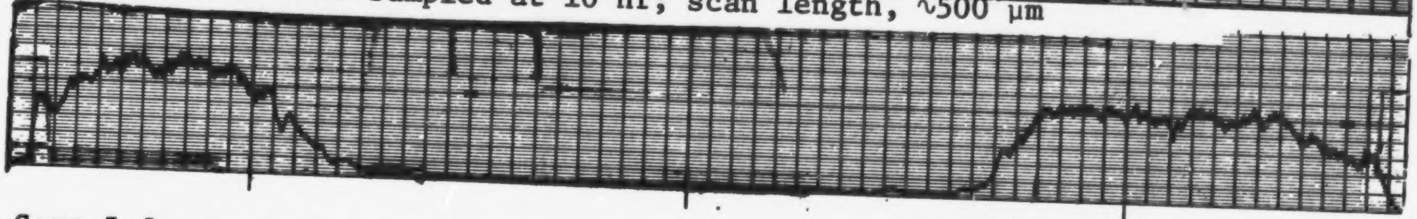
Scan 2 for particle sampled at 6 hr; scan length, ~600 μm



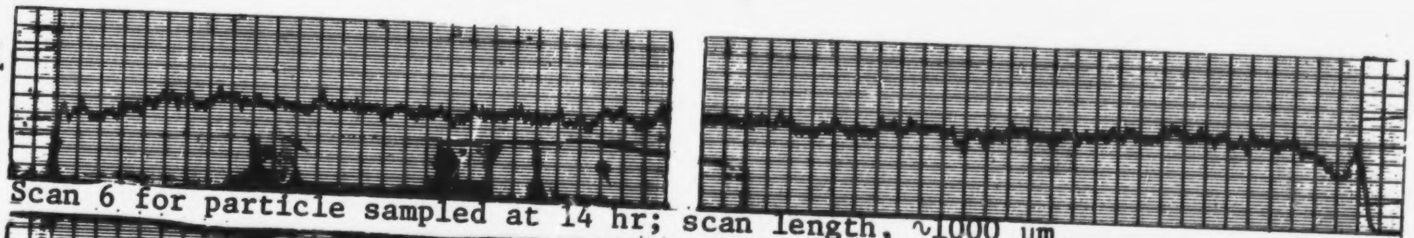
Scan 3 for particle sampled at 6 hr; scan length, ~1000 μm



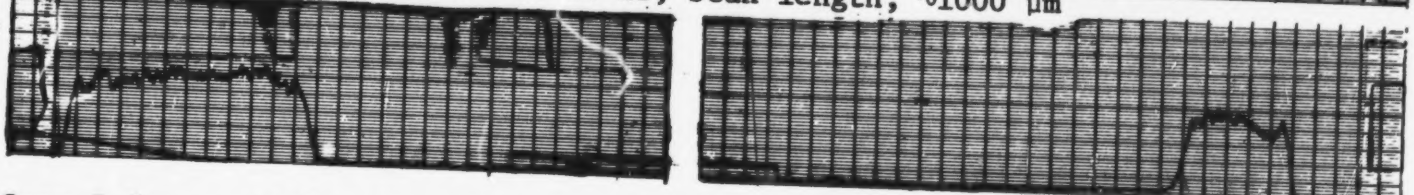
Scan 4 for particle sampled at 10 hr; scan length, ~500 μm



Scan 5 for particle sampled at 10 hr; scan length, ~600 μm

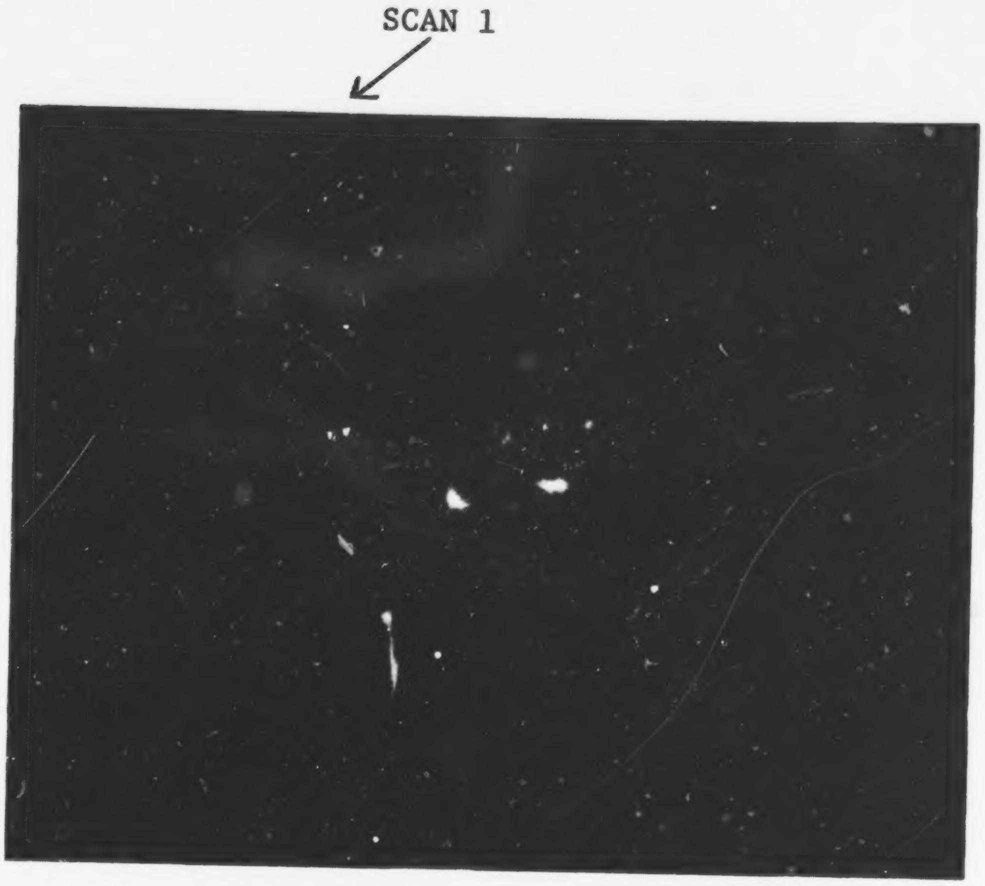


Scan 6 for particle sampled at 14 hr; scan length, ~1000 μm



Scan 7 for particle sampled at 14 hr; scan length, ~1000 μm

Fig. 11. Electron Microprobe Traces Showing Relative Sulfur Levels in Sulfated Particles, Experiment PB-3



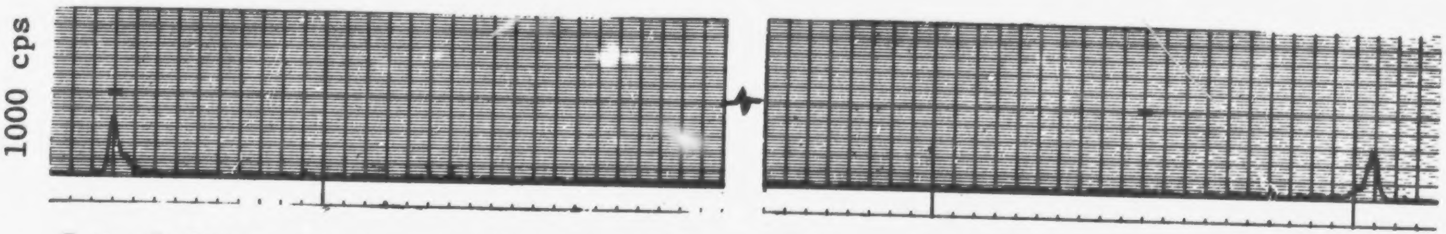
x50

Fig. 12. Photomicrograph of Particle Examined in Scan 1, Experiment PB-3

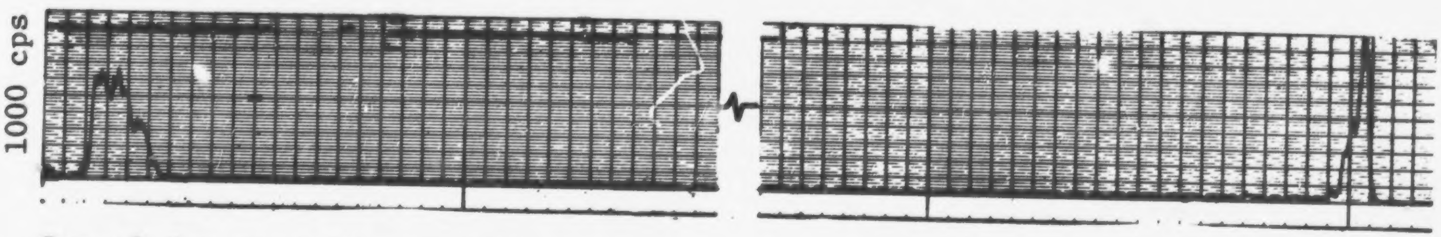
Table 8. Extent of Sulfation of Bed Particles as a Function of Reaction Time, Experiments PB-3 and PB-7

Elapsed Time (hr)	Micro-probe Scan	S (wt %)	Ca (wt %)	Ca/S Mole Ratio	% Sulfated
Experiment PB-3					
2	Yes	3.1	62.8	16	5.5
6	Yes	8.4	48.6	4.6	8.5
10	Yes	11.5	41.8	2.9	29.3
14	Yes	12.7	37.9	2.4	33
31	No	11.2	38.7	2.8	28
Experiment PB-7					
2	Yes	2.8	59.5	17	4.5
8	Yes	4.0	57.5	12	7.5

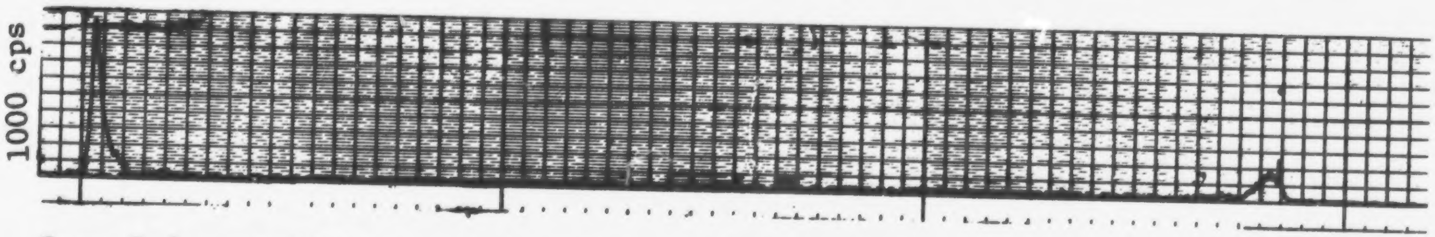
Microprobe scans of particles from bed samples removed at 2, 4, and 8 hr are shown in Fig. 13. The microprobe scans for experiment PB-7 are distinctly different from those for experiment PB-3. Depth of sulfation of the particles was very limited, and increasing reaction time did not produce greater penetration. The level of sulfur concentration at the outer surface of the particles from PB-7 was about twice that in experiment PB-3, and is estimated to represent 100% conversion to $CaSO_4$. The total sulfation, however, was substantially less, as shown by the data in Table 8. The highest level of conversion to $CaSO_4$ in PB-7 was only about 8%.



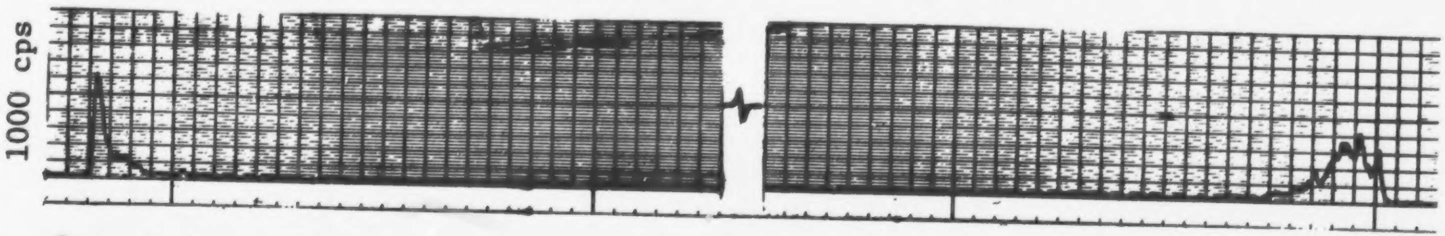
Scan 1 for particle sampled at 2 hr; scan length, ∿1200 μm



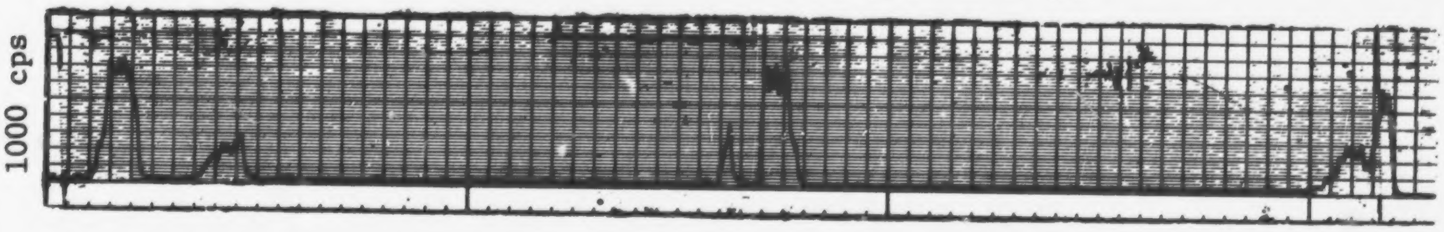
Scan 2 for particle sampled at 2 hr; scan length, ∿1000 μm



Scan 3 for particle sampled at 4 hr; scan length, ∿700 μm



Scan 4 for particle sampled at 8 hr; scan length, ∿1200 μm



Scan 5 for particle sampled at 8 hr; scan length, ∿800 μm

Fig. 13. Microprobe Scans of Sulfated Particles, Experiment PB-7

These results suggest that the mode of sulfur acceptance differed in the two experiments. In experiment PB-7, a nearly impenetrable sulfate shell built up that limited further sulfur pickup by the lime. In experiment PB-3, the sulfate shell was much more easily penetrated by SO_2.

Since the principal differences between the two experiments were the source of the SO_2 and the reaction environment (generation of SO_2 by combustion in experiment PB-3 and the absence of combustion in experiment PB-7), the presence of the combustion reaction apparently is important. These results strongly support the hypothesis that partial reducing conditions in the emulsion phase of the fluid bed can act to release bound SO_2, allowing it to be transported deeper into the lime particles.

2. Laboratory-Scale Experiments--Reduction of Sulfated Limestone

As was stated earlier (ANL/ES/CEN-1002, pp. 50-52), it has been observed that when natural gas is burned in a partially sulfated bed of lime (without fresh limestone addition), SO_2 is released from the bed at temperatures as low as 1650°F; yet in the absence of combustion, decomposition of $CaSO_4$ is known to occur only at much higher temperatures (>2000°F). A chemical reaction that would release SO_2 from sulfated lime is the following:

$$CaSO_4 + CO = CaO + CO_2 + SO_2 \qquad (16)$$

Two intermediate reactions control the rate of this reaction:

$$1/4\ CaSO_4 + CO = 1/4\ CaS + CO_2 \qquad (17)$$

$$3/4\ CaSO_4 + 1/4\ CaS = CaO + SO_2 \qquad (18)$$

The equilibria for these reactions are discussed in Section IV of this report.

Laboratory-scale experiments were performed to determine the effect of CO on the sulfation reaction and to investigate the use of CO in a regeneration step to remove SO_2 from sulfated lime (discussed further in Section IV). The procedure consisted of exposing a mixture of partially sulfated lime and particulate alumina in a vertical fixed-bed reactor to a mixture of gases that included CO and measuring the SO_2 content of the effluent gas. The partially sulfated lime was bed material from a bench-scale fluidized-bed coal combustion experiment (DUO-1) and typically would have a CaO conversion to $CaSO_4$ of about 30%. In each experiment, 200 g of the bed material was dispersed in an equal volume of refractory alumina spheres having an average diameter of somewhat less than 1/8 in. The mixture of lime bed material and alumina balls was supported on a 3- to 4-in. layer of alumina balls of the same size. A similar quantity of alumina balls was placed on top of the section containing the bed material.

In an experiment, the reactor was heated to the selected temperature with only nitrogen flowing through the reactor. When the selected reaction temperature was reached, a gas mixture containing CO, CO_2, H_2O, and N_2 was admitted to the reactor at a flow rate of about 4 liters/min. Water (∿3 vol %) was added to the CO-CO_2-N_2 mixture by passing it through a bubbler at room temperature. The effluent gas phase was analyzed for CO, CO_2, and SO_2; at the end of the experiment, the solid phase was submitted for analysis for total sulfur, $SO_3^=$, and $S^=$ content.

Four experiments (Mech-1 to -4) were performed. The initial stage of each experiment was the treatment with CO-CO_2-H_2O mixture in nitrogen, described above. Additionally, as the final stages of Mech-2 and -3, air was passed through the reactor to react with any CaS present in the bed.

The SO_2 and CO concentrations in the effluent gas during Mech-1 are shown in the plots of Fig. 14. During the initial period when only nitrogen was passed through the reactor, SO_2 was evolved. The concentration of SO_2 peaked at about 4200 ppm within 1/2 hr as the temperature was increased from 1500 to 1700°F, then fell to about 200 ppm after an additional 1/2 hr at 1700°F, staying at that level until the CO-containing gas was admitted several hours later. A possible explanation for the large evolution of SO_2 during the nitrogen flow period is decomposition of calcium sulfite ($CaSO_3$), which might have been an intermediate reaction product on the surface of the lime particles. The sulfite has a much lower decomposition temperature than does the sulfate. Another possibility is that reducing agents such as carbon or hydrocarbons in the bed may have reduced the $CaSO_4$.

When CO-containing gas was admitted at about 1750°F, SO_2 was evolved immediately. Its concentration in the gas phase rose to about 6000 ppm. However, dependence of the SO_2 concentration on the CO concentration, predicted by equilibrium and phase rule considerations (see Section IV), was not observed. The presence or absence of water vapor in the reacting gas did affect SO_2 evolution; the SO_2 concentration dropped to about 3000 ppm when feeding of H_2O in the reaction gas mixture was stopped.

The results of gas phase analysis for the second experiment, Mech-2, are shown in Fig. 15. In this experiment, the initial reaction temperature was 1650°F. During the period when only nitrogen was passing through the reactor, SO_2 evolution was noted but the initial peak was much lower than in Mech-1 at 1750°F. When the reducing gas (10% CO, 15% CO_2, ~3% H_2O, and N_2) was admitted to the reactor, a spike was noted in the SO_2 evolution trace, but then the SO_2 concentration rapidly dropped to about 500 ppm. Increasing the reaction temperature to 1750°F did not greatly change SO_2 evolution. On the chance that reaction 17 was dominating the process and CaS was being formed, the reducing gas mixture was replaced with air to convert the CaS to CaO and SO_2 according to the reaction

$$CaS + 3/2\ O_2 = CaO + SO_2. \qquad (19)$$

This change brought about an immediate increase in the SO_2 concentration to somewhat more than 4 vol %. The high rate of SO_2 evolution continued for about 10 min, then the SO_2 level dropped gradually to several thousand ppm, indicating CaS was present.

In Mech-3, the portion of the experiment in which reducing gas was fed was performed at 1500°F to determine if the formation of CaS would be favored. This reaction produced little SO_2 during either the 1500°F reducing step or the air oxidation step at temperatures up to 1800°F. This result indicates that a temperature of 1500°F is too low for reaction 17. In experiment Mech-4, with reducing gas fed at 1600°F, similar SO_2 data were obtained as at 1750°F in experiment Mech-2.

In general, these laboratory-scale experiments show that SO_2 can be released under reducing conditions. When the temperature is about 1600°F, CaS is formed instead of SO_2. At 1500°F, no reaction apparently occurs. The results lend support to the hypothesis that in the combustor, $CaSO_4$ is cyclically reduced to CaS which is then oxidized to generate SO_2. This reaction could contribute to SO_2 penetration into the lime particle and could limit SO_2 removal at high combustion temperatures. The reduction mechanism may still be operative at a fluidized-bed temperature of 1500°F, since particle temperatures are known to exceed the measured bed temperatures.

In addition, these results suggest that recovery of SO_2 by a two-step cycle employing reactions 17 and 19 is feasible at relatively moderate temperature. These reactions are also favorable in that they are not repressed by high-pressure operation. In fact, reaction 19 would be enhanced by operation at high pressure.

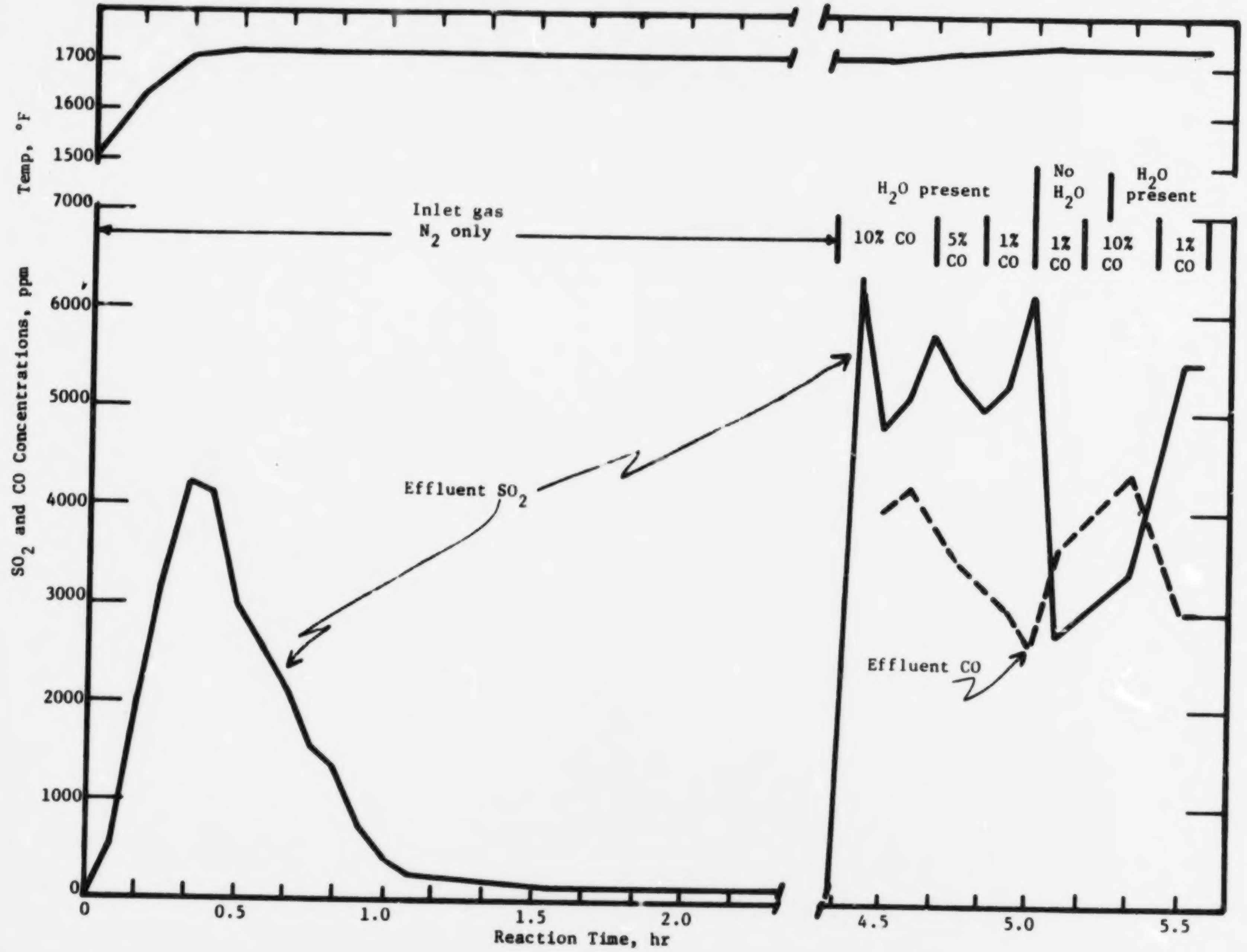


Fig. 14. Reaction of Sulfated Lime with CO-CO$_2$-H$_2$O-N$_2$ Mixtures, Experiment Mech-1

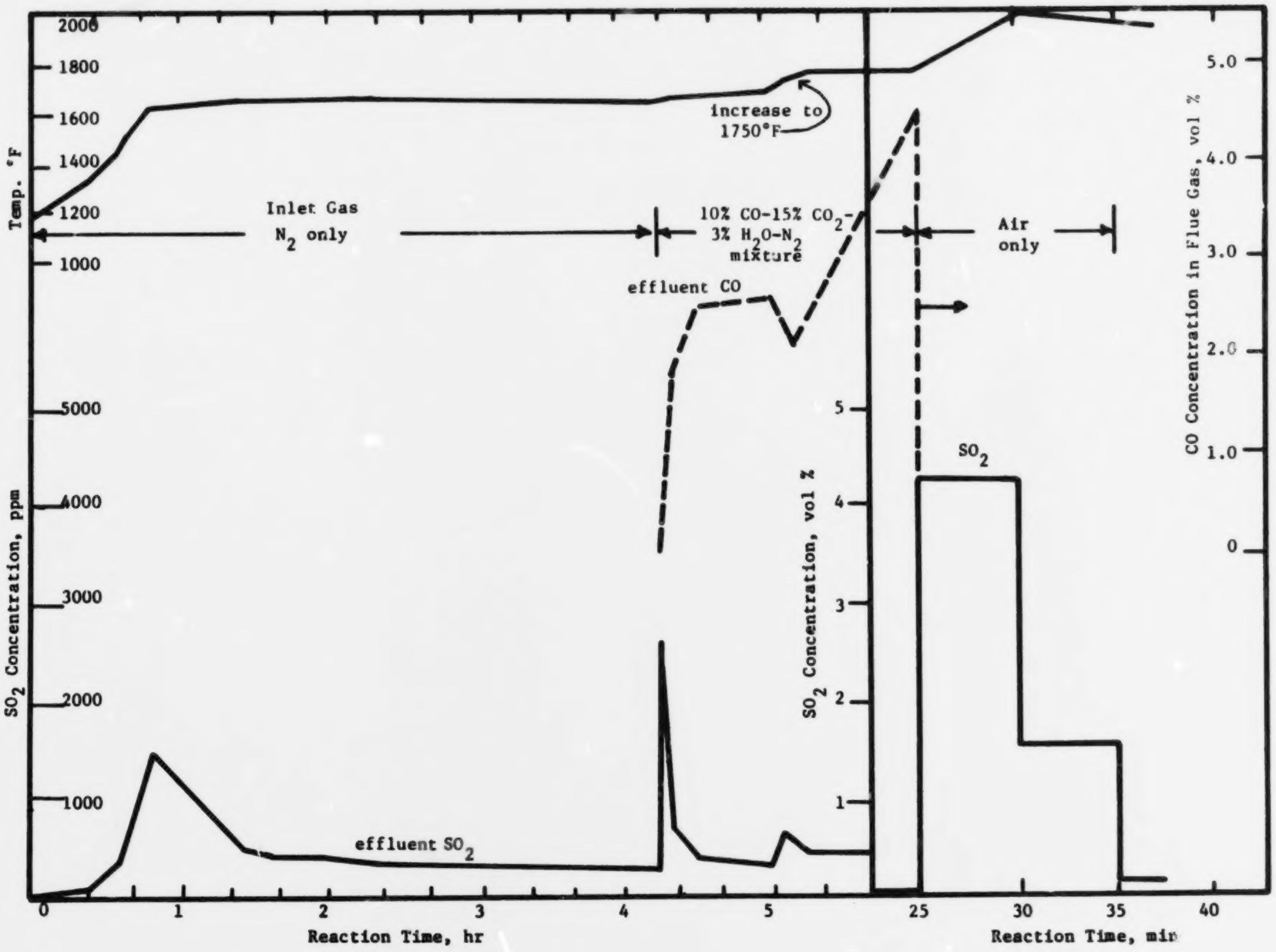


Fig. 15. Reaction of Sulfated Lime with CO-CO$_2$-H$_2$O-N$_2$ Mixtures Followed by Reaction with Air, Experiment Mech-2

IV. REGENERATION OF CaO FROM $CaSO_4$*

Regeneration of partially sulfated lime would be desirable (1) for recycle of the lime, thereby reducing the solids waste burden imposed by the sulfur-removal process and (2) to recover a sulfur value as sulfuric acid or elemental sulfur.

Listed below are chemical reactions for a process to regenerate CaO from $CaSO_4$ using CO reductant (H_2 is an alternative reductant):

$$CaSO_4(s) + CO(g) \rightleftarrows \underset{x_1}{CaO(s)} + \underset{x_1}{CO_2(g)} + \underset{x_1}{SO_2(g)} \tag{20}$$

$$1/4\ CaSO_4(s) + CO(g) \rightleftarrows \underset{1/4\ x_2}{1/4\ CaS(s)} + \underset{x_2}{CO_2(g)} \tag{21}$$

$$3/4\ CaSO_4(s) + 1/4\ CaS(s) \rightleftarrows CaO(s) + SO_2(g) \tag{22}$$

Reactions 20 and 22 are endothermic, while reaction 21 is exothermic. Since this system is considered to be in equilibrium, the phase rule can be applied:

$$P + F = C + 2 \tag{23}$$

where P = number of phases at equilibrium
F = number of degrees of freedom
C = number of components

There are four components and four phases ($CaSO_4$, CAO, CaS, and the gas phase), giving a total of two degrees of freedom. However, there is a restriction caused by the fixed ratio between calcium and sulfur in the initial material ($CaSO_4$). This cancels one degree of freedom. This could be temperature, or pressure, or one mole fraction in the gas phase. Obviously this univariant system exists only under very limited conditions. Under other conditions other reactions will occur. The range of conditions will be expanded in further work.

Only two of the reactions 20, 21, and 22 are independent since any two reactions can be combined to give the third. Therefore, reactions 20 and 21 were arbitrarily chosen to make the equilibrium calculations.

Let x_1 = moles of each product formed by reaction 20 at equilibrium

x_2 = moles of each product formed by reaction 21 at equilibrium

y_1 = mole fraction CO in feed gas

y_2 = mole fraction CO_2 in feed gas

y_3 = mole fraction inert gases (N_2) in feed gas.

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*We are indebted to Professor Scott Wood of the Illinois Institute of Technology for his advice and assistance in these equilibrium calculations.

For one mole of entering gas, the equilibrium composition for each compound is given in Table 9. From this,

$$K_{P_1} = \frac{P_{CO_2}\ P_{SO_2}}{P_{CO}} = \frac{\left(\frac{y_2 + x_1 + x_2}{1 + x_1}\right)\left(\frac{x_1}{1 + x_1}\right)\pi^2}{\frac{y_1 - x_1 + x_2}{1 + x_1}\ \pi} \qquad (24)$$

and $$K_{P_2} = \frac{P_{CO_2}}{P_{CO}} = \frac{\frac{y_2 + x_1 + x_2}{1 + x_1}\ \pi}{\frac{y_1 - x_1 - x_2}{1 + x_1}\ \pi} \qquad (25)$$

which reduces to $$K_{P_1} = \frac{(y_2 + x_1 + x_2)(x_1)\ \pi}{(y_1 - x_1 - x_2)(1 + x_1)} \qquad (24a)$$

and $$K_{P_2} = \frac{y_2 + x_1 + x_2}{y_1 - x_1 - x_2} \qquad (25a)$$

and finally to $$K_{P_1} = K_{P_2}\ \frac{\pi\ (x_1)}{(1 + x_1)} \qquad (26)$$

where π = total pressure

Equation 26 is consistent with the phase rule since the fixing of two degrees of freedom (temperature, pressure, or mole fraction SO_2) provides an invariant system at equilibrium.

A. Effect of Pressure

An important variable in the regeneration process is the total pressure of the system. It may be desirable that the regeneration cycle operate at the same pressure as the combustor since this would facilitate coupling the regenerator to the combustor for a continuous mode of operation. Therefore, a high-pressure process is envisioned for both fluidized-bed combustion and regeneration. With a high-pressure process either the throughput with smaller equipment will be equivalent to that obtained at 1 atm with large equipment, or the throughput will be increased in equipment having the same size as atmospheric units. The effect of pressure--especially on the concentration of SO_2 in the gas phase--is being evaluated.

TABLE 9. Equilibrium Composition for CO and CO_2 during Regeneration of $CaSO_4$

Basis: 1 mole of feed gas

	Inlet Composition (mole fraction)	Equilibrium Conversion (moles)	Total Moles at Equilibrium
CO	y_1	$- x_1 - x_2$	$y_1 - x_1 - x_2$
CO_2	y_2	$+ x_1 + x_2$	$y_2 + x_1 + x_2$
SO_2	0	$+ x_1$	$+ x_1$
N_2	y_3	0	y_3
	1.00	$+ x_1$	$1.00 + x_1$

Equation 26 has been used to calculate the equilibrium pressure of SO_2 at system pressures of 1 and 10 atm over the temperature range 1400 to 2000°F (Fig. 16). It is important to note that the SO_2 mole fraction is inversely proportional to the total system pressure at any fixed temperature and that on the basis of equilibrium considerations, pressurized regeneration of $CaSO_4$ is not attractive from this standpoint. The equilibrium calculations indicate that the expected SO_2 yield at 10 atm and 1950°F would be no greater than 4 vol %, a relatively low concentration if the gases are to be fed to a Claus plant for recovery of sulfur.

A reaction scheme proposed by Squires and Graff[12] is under consideration but has not yet been studied experimentally. In their reaction scheme, partial reduction of $CaSO_4$ to CaS with hydrogen is followed by the reaction of CaS with CO_2 and H_2O to form $CaCO_3$ and H_2S as shown in the following reaction:

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S$$

This reaction is reported to occur at 1100°F and to be favored by high pressure.

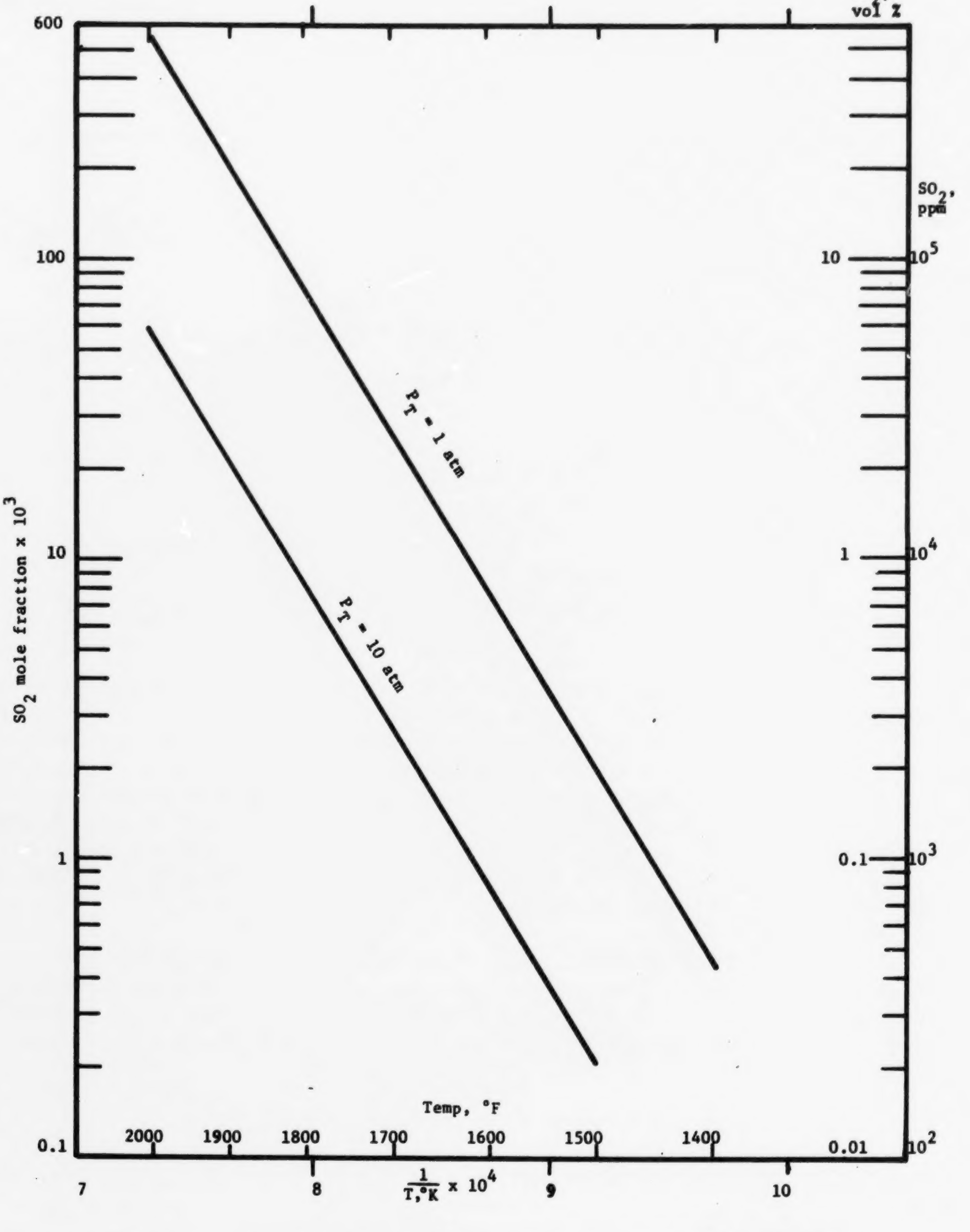

Fig. 16. Equilibrium Mole Fraction SO_2 at 1400-2000°F

$CaSO_4 + CO = CaO + CO_2 + SO_2$

$1/4\ CaSO_4 + CO = 1/4\ CaS + CO_2$

$3/4\ CaSO_4 + 1/4\ CaS = CaO + SO_2$

B. Experimental

Initial laboratory-scale experimental work to evaluate the effect of pressure has been on the reduction of $CaSO_4$ in a fluid bed, using CO as the reductant. Two experiments were performed at 1950°C and pressures of 1 and 10 atm. The gas velocity was 2 ft/sec, sufficient to fluidize the partially sulfated and calcined lime beds. The first of the regeneration experiments was performed at 1-atm pressure (Regen-5) and the second at 10-atm pressure (Regen-9).

The laboratory-scale regeneration reactor used in these experiments is shown diagrammatically in Fig. 17. The 2-in.-dia vertical tube reactor is constructed of type 316 stainless steel. It is about 5 ft long, with the lower 2 ft enclosed by electric furnaces. The upper part of the reactor is insulated to reduce heat loss.

The starting fluid-bed material (from previous experiments) consisted of 628 g of sulfated limestone containing 10.7 wt % sulfur in Regen-5 and consisted of 1169 g of sulfated limestone containing 10.0 wt % sulfur in Regen-9. Nitrogen flowed through the reactor at incipient fluidization velocity as the reactor was heated by electric furnaces to about 1700°F. To increase the temperature to 1950°F, CO was burned. At this temperature, a gas mixture consisting of 10 vol % CO-20 vol % CO_2 and the remainder nitrogen and oxygen (when required) was admitted to the reactor. The reactor effluent gas stream was passed through a filter chamber to remove entrained solids, through a pressure-reducing stage if necessary, and then at nearly atmospheric pressure to the gas-sampling manifold for SO_2, CO, CO_2, and O_2 analysis. The solid residue in the reactor was analyzed for total sulfur and for sulfur present as sulfide.

During the experiment at 1 atm (Regen-5), the SO_2 concentration in the reactor effluent rose to 3 to 4 vol % within the first minute of reaction and then decreased during a 20-min period to essentially zero. The CO concentration in the effluent was low, less than 5000 ppm, during the period of peak SO_2 evolution and then rose rapidly as SO_2 evolution subsided. The solid residue contained 3.2 wt % sulfur, of which 2.8 wt % was sulfide (CaS). The results show that about 80% of the sulfur contained in the original sample was converted to SO_2. Nearly 90% of the sulfur in the residue was sulfide, indicating that the reaction had stopped short of complete conversion to SO_2 because of an unfavorable CaS to $CaSO_4$ ratio.

During experiment Regen-9 (performed at a total pressure of 10 atm), control of the temperature in the fluidized bed was difficult and sporadic at best, apparently because of partial caking of the bed soon after the $CO\text{-}CO_2\text{-}O_2\text{-}N_2$ mixture was fed.

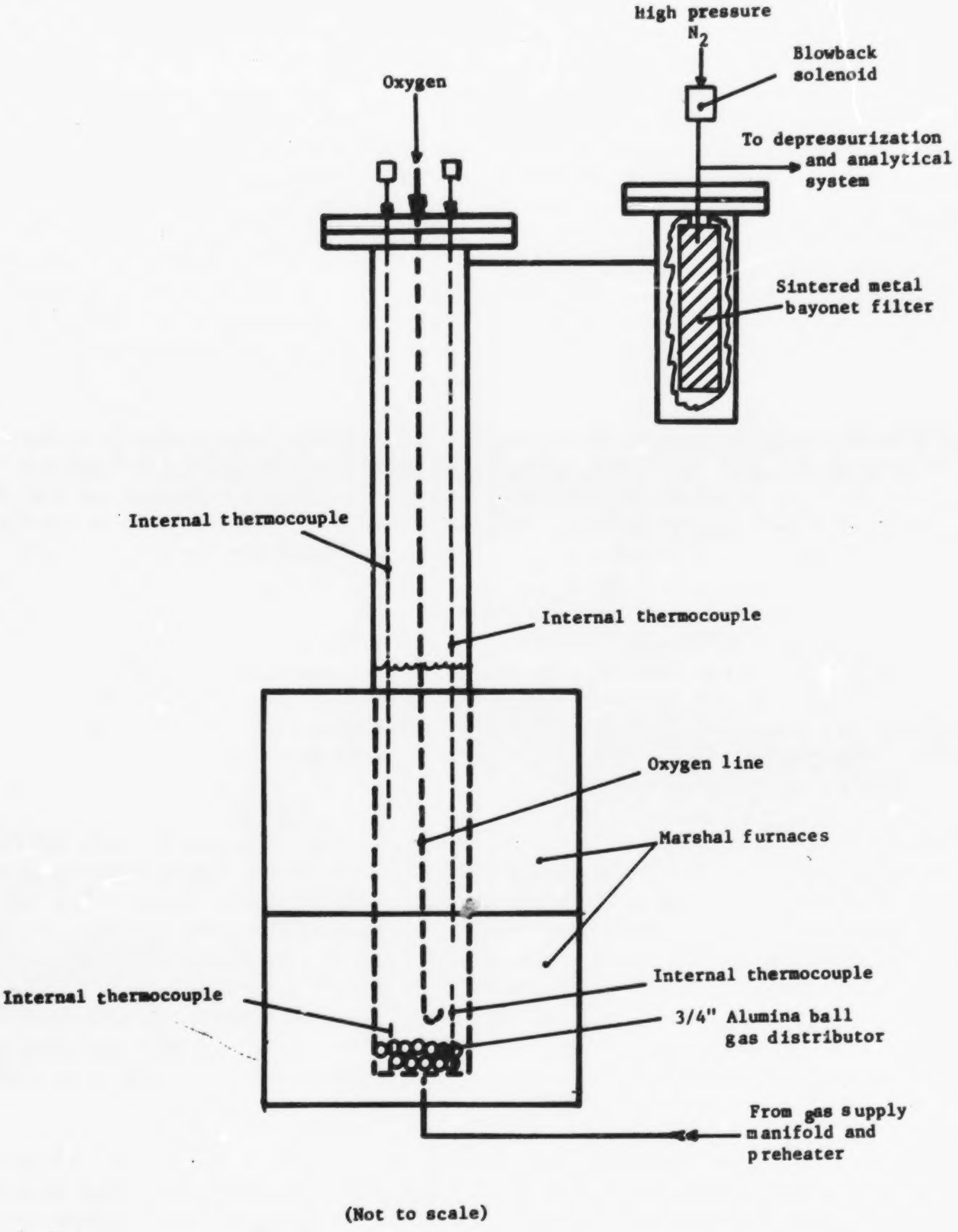
High pressure N2
Blowback solenoid
Oxygen
To depressurization and analytical system
Sintered metal bayonet filter
Internal thermocouple
Internal thermocouple
Oxygen line
Marshal furnaces
Internal thermocouple
Internal thermocouple
3/4" Alumina ball gas distributor
From gas supply manifold and preheater
(Not to scale)

Fig. 17. Fluidized-Bed Regenerator (2-in. dia)

V. MODELLING STUDIES, SO_2 REMOVAL

(Lowell B. Koppel[*])

The process of reducing the emissions of SO_2 by heterogeneous reaction with additive limestone particles in a fluidized-bed combustor is mathematically complex. The objective of this study is to devise a mathematical model which is convenient for use and which yields reasonably accurate predictions of removal level and predicts how SO_2 removal is affected by typical operating variables. To achieve this, several assumptions regarding the process are made.

A. Model and Assumptions

Figure 18 illustrates certain of the model assumptions. In accord with current theory on flow through fluidized beds, the bed is assumed to be divided into two phases--a particulate phase through which gas flows at the minimum fluidizing velocity, and a bubble phase which contains all the gas flow in excess of that required for incipient fluidization of the bed. The gas in the particulate phase is in plug flow, having uniform SO_2 concentration across any horizontal plane. Additive particles in the particulate phase are perfectly mixed so that the entire particulate phase is at a uniform temperature. As the additive particles in the bed absorb SO_2, their average reactivity (expressed in terms of first-order reaction velocity constant) is assumed to decrease linearly with the extent of SO_2 absorption. Gas is continuously exchanged between the bubble and particulate phases.

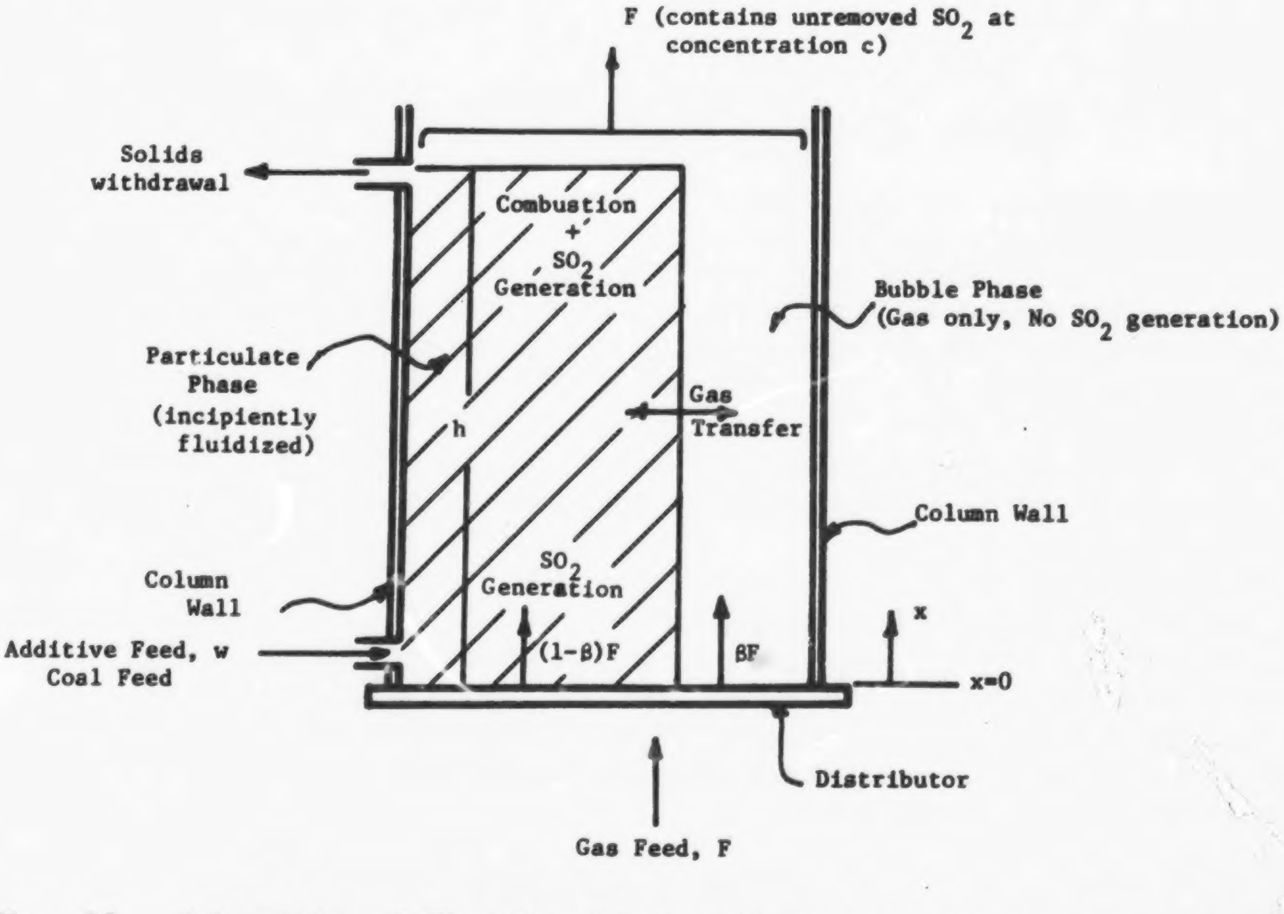
F (contains unremoved SO2 at concentration c)
Solids withdrawal
Combustion + SO2 Generation
Bubble Phase (Gas only, No SO2 generation)
Particulate Phase (incipiently fluidized)
h
Gas Transfer
Column Wall
SO2 Generation
Column Wall
x
Additive Feed, w
Coal Feed
(1-β)F
βF
x=0
Distributor
Gas Feed, F

Fig. 18. Schematic of Fluidized Bed, Illustrating Model Assumptions

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[*] L. B. Koppel, Purdue University, consultant to the Chemical Engineering Division, Argonne National Laboratory.

B. Model Equations

With these assumptions, and with a group of curves (to be discussed below) to describe the SO_2 generation pattern, equations can be derived to predict SO_2 removal R, as well as particle consumption C. Numerical study of these equations showed that the effects of gas bubbles bypassing the bed could be omitted. Hence, the equations for SO_2 removal R and particle consumption C are reproduced here only for the case of no bubble flow ($\beta=0$).

$$R = 1 - \frac{\alpha[e^{-\alpha} - e^{-H(1 - \frac{R}{r})}]}{(1 - e^{-\alpha})[H(1 - \frac{R}{r}) - \alpha]} \qquad (27)$$

$$C = \frac{R}{r} \qquad (28)$$

Symbols are defined in Table 10, and details of the derivation have been presented in another document.[13] The values of r and H are obtained from operating data and supporting kinetic data; α is a shape parameter describing the SO_2 generation pattern. Given values of the parameters, α, r, and H, Equation 27 is solved iteratively for SO_2 removal, R. Equation 28 then yields the particle consumption C.

Figure 19, previously published in ANL/ES/CEN-1002, is printed here to show the relationship of α to the generation pattern. At higher values of α, relatively more SO_2 is generated near the bed entrance. The equation which generates the curves of Fig. 19 is

$$\text{Relative local rate of } SO_2 \text{ generation} = \frac{\alpha e^{-\alpha x/h}}{1 - e^{-\alpha}}$$

Postive values of α imply that most SO_2 is generated near the entrance; negative values imply that most SO_2 is generated near the exit. Uniform SO_2 generation corresponds to $\alpha = 0$; generation of all SO_2 at the bed entrance corresponds to $\alpha \rightarrow \infty$. Figure 19 illustrates the diversity of generation patterns which can be obtained simply by changing the single parameter α; it is this factor that leads to selection of this particular family of generation patterns for inclusion in the model.

To calculate H, it is necessary to know K, the reaction velocity constant for fresh additive particles. Typical laboratory kinetic data might be in the form of Fig. 20.[6] A batch of additive CaO is exposed to SO_2 at a known concentration c_o and at the temperature and pressure anticipated during combustion conditions. The moles of SO_2 absorbed per pound of CaO are plotted against time. The parameter K is obtained from the initial slope of the curve.

$$K = \frac{\text{Initial Slope}}{c_o}$$

TABLE 10. Definition of Symbols

b_1,b_2,b_3,b_4,b_5 = model fitting constants

C = particle consumption, y/y_e

c = exit concentration of SO_2, moles/volume

c_o = concentration of SO_2 used in laboratory test

F = total gas flow, volume/time

f = ratio of actual to ideal absorption capacity, y_e/y_s

H = bed inventory parameter, KW/F

h = fully expanded bed height

K = value of reaction velocity constant for fresh additive, volume/(time)(weight of additive)

M = Ca/S mole ratio fed to fluidized bed

R = fractional removal of SO_2, $1 - Fc/S$

r = effective feed ratio of additive to SO_2, wy_e/s

S = total rate of generation of SO_2, moles/time

T = operating temperature of fluidized bed, °F

W = total weight (reacted + unreacted) of additive in fluidized bed

w = feed rate of fresh additive, mass/time. Also equals removal rate of exhausted additive.

x = distance above bed entrance.

y = average SO_2 absorbed by additive particles in bed, moles SO_2/mass additive

y_c = ultimate SO_2 absorption capability of additive particles, moles SO_2/mass additive

y_s = stoichiometric SO_2 absorption capability of additive particles, moles SO_2/mass additive

z = x/h

α = shape parameter describing the SO_2 generation pattern; higher values of α correspond to relatively more SO_2 generation near the bed entrance.

β = fraction of total gas feed going to bubble phase

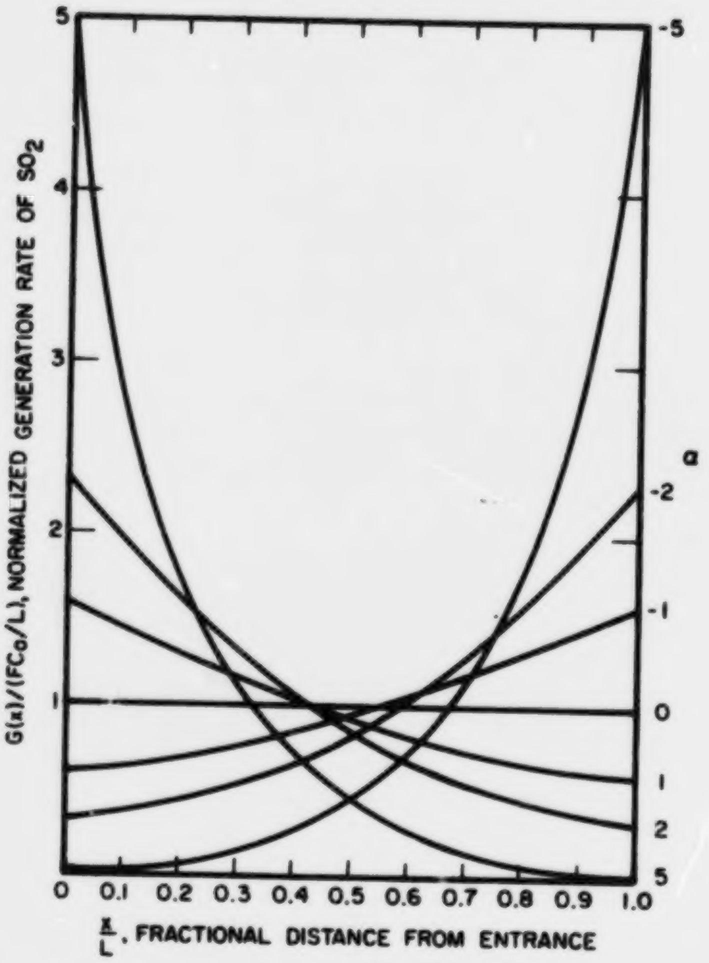

Fig. 19. Normalized Generation Rate of SO_2 as a Function of Fractional Bed Height

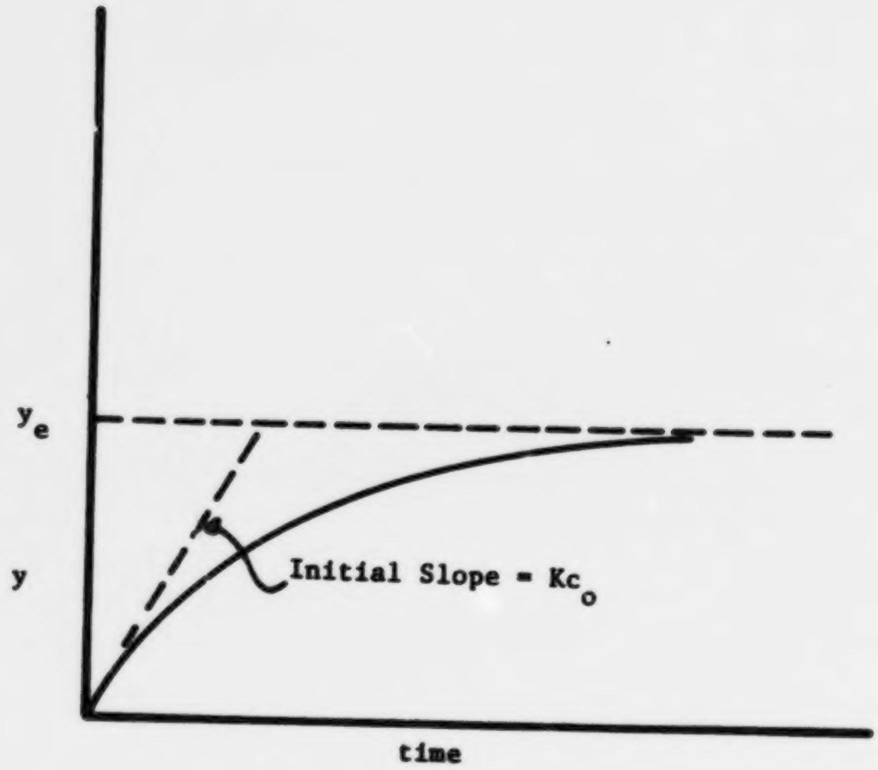

Fig. 20. Typical Laboratory Kinetic Data and Interpretation

In addition, y_e is obtained as the asymptotic value of y, as shown.
Example:

To illustrate the model, some typical calculations will be made. Consider the following operating data for a fluidized-bed combustor:

$w = 0.8$ lb CaO/hr
$W = 16$ lb CaO
$S = 0.006$ mole SO_2/hr
$F = 1000$ cfh

and the following kinetic data:

Initial Slope = 0.04 mole SO_2/(lb CaO)(hr)
$y_e = 0.013$ mole SO_2/lb CaO
$c_o = 4 \times 10^{-6}$ mole SO_2/ft^3

The calculations then proceed as follows:

$$r = \frac{wy_e}{S} = \frac{(0.8)(0.013)}{(0.006)} = 1.7$$

$$K = \frac{\text{Initial Slope}}{c_o} = \frac{0.04}{4 \times 10^{-6}} = 10^4 \frac{ft^3}{(\text{lb CaO})(\text{hr})}$$

$$H = \frac{KW}{F} = \frac{10^4(16)}{10^3} = 160$$

These values are used in Eqs. 27 and 28 to compute predicted values of R and C. With an H of 100 and values of α of -10, -5, -2, 0, 2, and 5, SO_2 removals are 88, 93, 97, 99, 99, and $\sim$100%. Particle consumptions may be calculated by dividing the removals by 1.7, the value of r.

Note from this example that r is the effective feed ratio of additive to SO_2. Thus, based on the stoichiometry of one mole of SO_2 to one mole of CaO, the theoretical ultimate value of y is 0.018, and the theoretical stoichiometric feed rate is (0.8)(0.018)/(0.006) = 2.4. This figure is reduced to an effective value of 1.7 because CaO does not absorb the stoichiometric quantity of SO_2.

C. Effects of Parameters on SO_2 Removal and Particle Consumption

Figures 21-23 present illustrative values, calculated as described in the preceding section, of SO_2 removal and particle consumption for various values of r, α, H. In each figure, the normalized bed inventory variable H is constant. Removal, R, and consumption, C, are plotted against additive-to-SO_2 feed ratio r at various values of the SO_2 generation pattern shape parameter α.

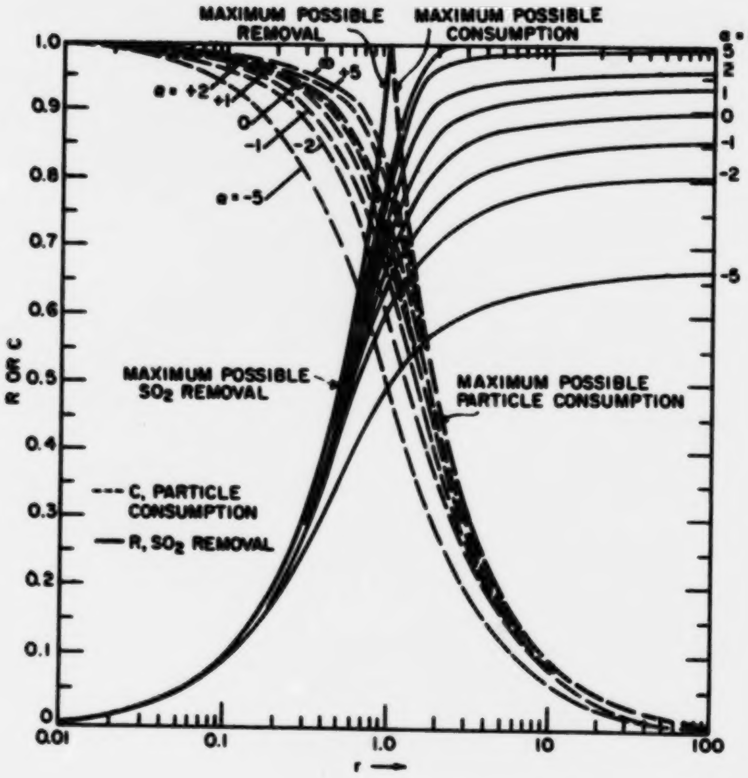

Fig. 21. Calculated SO_2 Removal and Particle Consumption, H = 10

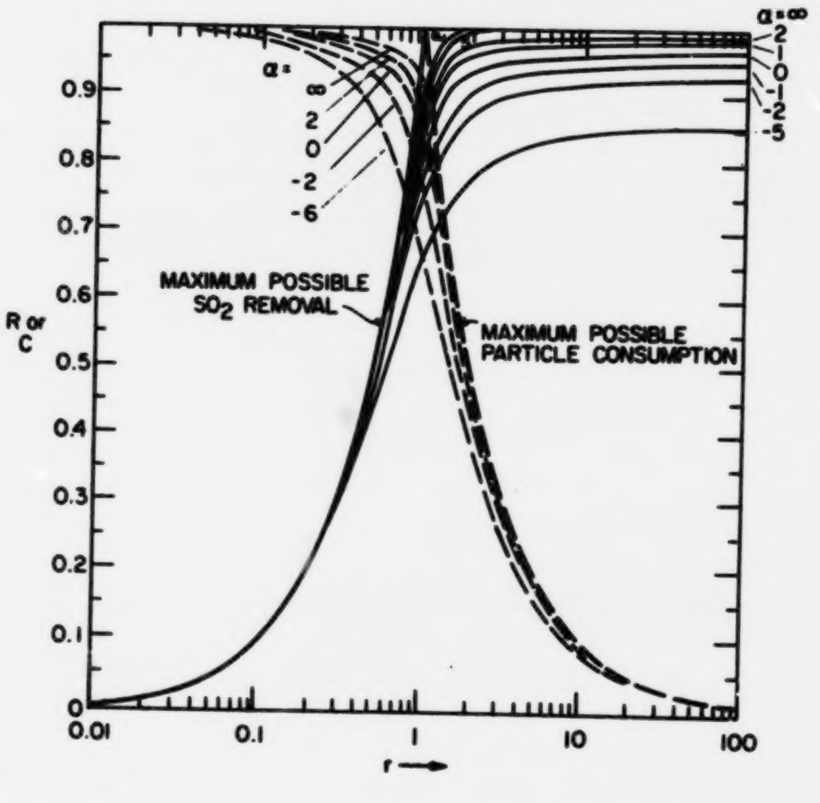

Fig. 22. Calculated SO_2 Removal and Particle Consumption, H = 30

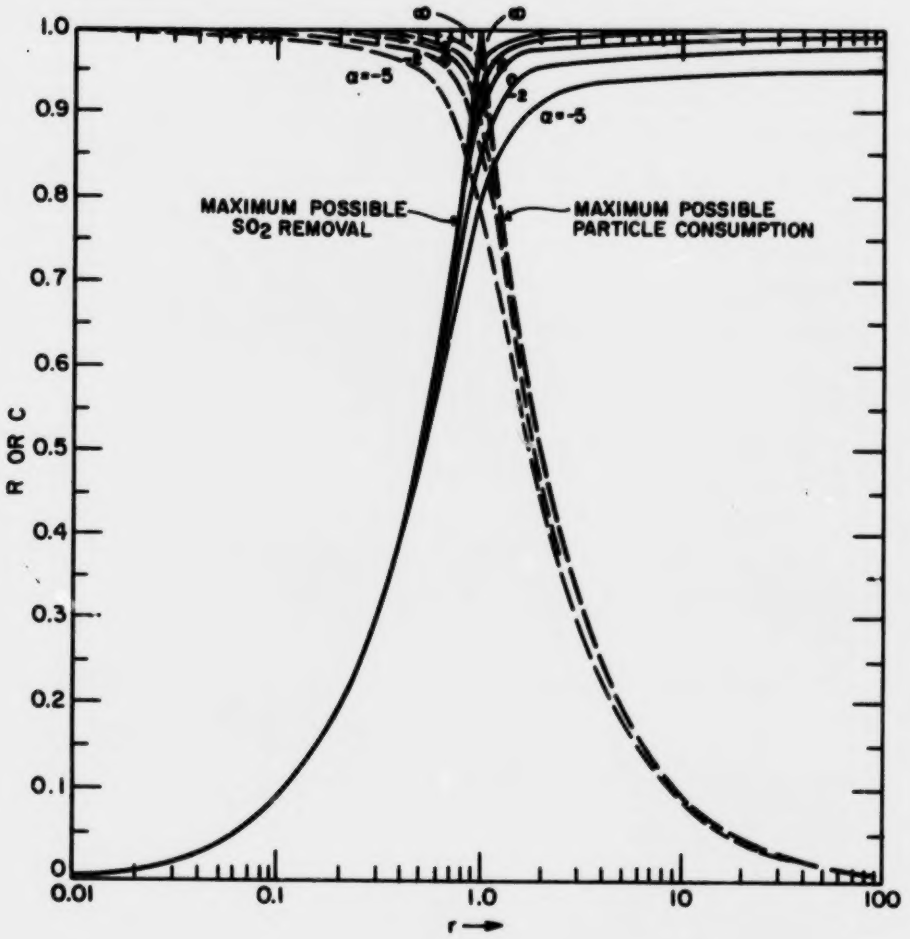

Fig. 23. Calculated SO_2 Removal and Particle Consumption, H = 100

As r is increased beyond approximately 10, removal does not significantly increase with r in a given graph. This is because the bed reactivity H is constant. At r = 10, the bed essentially contains only highly reactive, unconsumed particles. This represents the maximum possible bed reactivity and further increases in r would not be expected to improve SO_2 removal. Obviously, consumption is so low at these higher values of r that even the asymptotic value cannot be economically attained.

For an additive-poor bed, H = 10, the effect of SO_2 generation pattern is quite strong. However, as the bed inventory is increased, α becomes less important.

Also shown in each of Figs. 21-23 are two curves, one representing maximum possible values of particle consumption and the other maximum possible SO_2 removals. Since r is the effective additive to SO_2 feed ratio, maximum possible removal occurs at complete consumption (C = 1) if the value of r is less than unity, and maximum possible removal is unity if r exceeds unity. Similarly, maximum possible consumption occurs at complete removal (R = 1) for values of r greater than unity, and is unity for values of r less than unity. Thus,

$$R_{max} = r \text{ and } C_{max} = 1 \text{ if } r < 1$$

$$R_{max} = 1 \text{ and } C_{max} = \frac{1}{r} \text{ if } r > 1$$

The curves in Figs. 21-23 show how closely ideal conditions are approached at different values of α.

Figure 24 shows the effect of bed inventory on SO_2 removal and particle consumption. The additive-to-SO_2 feed ratio r is held fixed at unity, and R and C (which are equal when $r = 1$) are plotted against H for various values of α. Clearly, additive-rich beds are desirable and a bed as rich as $H = 1000$ (or an equivalent series of smaller beds) should give virtually complete SO_2 removal and particle consumption, regardless of the SO_2 generation pattern.

This analysis shows why knowledge of the kinetic parameters K and y_e is needed for rational design. Reasonable SO_2 removals apparently require operations with $r > 1$ and $H > 100$. Values of r and H depend not only on the corresponding operating variables--additive feed rate and additive inventory--but also on the kinetic parameters.

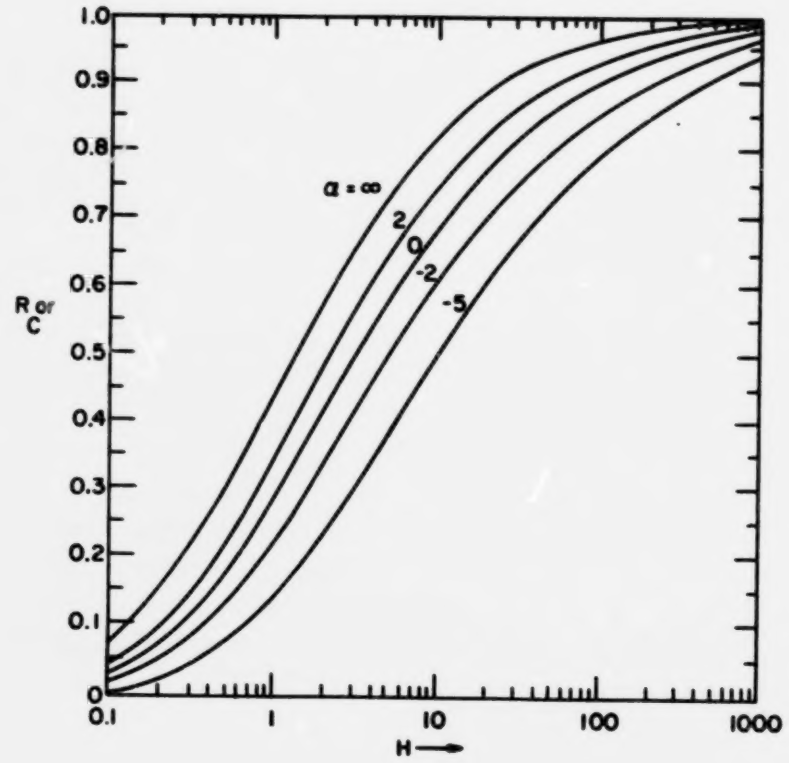

Fig. 24. Calculated SO_2 Removal and Particle Consumption, $r = 1$

D. Comparison of Model with Data

Further attention will be restricted to two specific SO_2 generation patterns. If all SO_2 is generated at the entrance to the bed, $\alpha \to \infty$ and Eq. 27 reduces to

$$R = 1 - e^{-H(1 - \frac{R}{r})} \qquad (29)$$

If the SO_2 is generated uniformly throughout the bed, $\alpha = 0$ and Eq. 27 reduces to

$$R = 1 - \frac{1 - e^{-H(1 - \frac{R}{r})}}{H(1 - \frac{R}{r})} \qquad (30)$$

The parameters H and r are related to the physical parameters by

$$H = \frac{KW}{F} \qquad (31)$$

$$r = \frac{wy_e}{S} \qquad (32)$$

However, if M is the Ca/S mole ratio fed to the column, then r can also be expressed as

$$r = Mf \qquad (33)$$

where the fraction f is defined by

$$f = \frac{y_e}{y_s} \qquad (34)$$

and is the ultimate SO_2 absorption capability of additive particles relative to the ideal stoichiometric absorption capability of the additive particles.

The reaction velocity constant K and the fraction f may depend on the temperature T at which the bed is operated. Two forms of this dependence were chosen for investigation:

$$\left.\begin{aligned} K &= b_1 + b_2\,(T + 460) + b_3\,(T + 460)^2 \\ f &= b_4 \end{aligned}\right\} \qquad (35)$$

and

$$\left.\begin{aligned} K &= b_1 + b_2\,(T + 460) \\ f &= b_4 + b_5\,(T + 460) \end{aligned}\right\} \qquad (36)$$

Thus, four models were investigated for fitting the experimental data.

Model 1 -- Eqs. 29 and 35
Model 2 -- Eqs. 29 and 36
Model 3 -- Eqs. 30 and 35
Model 4 -- Eqs. 30 and 36

A computer program was devised to find values of the fitted constants b_1, b_2, b_3, b_4, b_5 such that best (in the least-squares sense) agreement was obtained between values of R calculated from the model and those observed experimentally. A total of 45 runs were used as data to be fitted to the model. The ranges of experimental values covered were:

T	1325 to 1800°F
W	18 lb
F	458 to 1412 cfh
M	1.0 to 5.5

The results (Table 11) show that the standard error for each model is similar, in the range 10-11%. This standard error appears to be reasonable on the basis of inspection which showed some lack of reproducibility in the data. Thus, the fitting results do not allow determination of which SO_2 generation pattern is more realistic.

TABLE 11. Values of Fitted Constants Obtained by Model Fitting

Model	b_1	b_2	b_3	b_4	b_5	Standard Error of Prediction
1	-5153.4870	5.3025818	-0.00133601	0.49891591	-	10.3
2	-532.00413	0.32007391	-	0.34173206	-0.001462656	11.3
3	-13830.389	14.32897	-0.00362929	0.49500000	-	10.4
4	-1964.5366	1.1602147	-	3.0735411	-0.0013070000	11.3

VI. MISCELLANEOUS

A. Control of Chloride Emissions

Most U.S. coals contain a small amount of chloride that is emitted as hydrogen chloride when the coal is burned. Since lime is capable of reacting readily with hydrogen chloride, it was decided to examine, theoretically, the potential of several oxides and hydroxides for control of chloride emissions at the concentrations encountered in the fluidized-bed combustion process. This information might also be of value for application of fluidized-bed combustion to the incineration of chloride-bearing wastes such as polyvinyl chloride plastics.

The capability of a lime bed for removing hydrogen chloride from combustion gases would depend on the thermodynamic equilibrium of the reversible reaction

$$CaO + 2\ HCl \rightleftarrows CaCl_2 + H_2O$$

Calculated values of the equilibrium partial pressure of HCl with several oxides and hydroxides as a function of temperature at a partial pressure of water of 0.1 atm (approximately that in flue gas) are shown in Fig. 25. At a combustion temperature of 1550°F (1090°K), the equilibrium partial pressure of HCl with CaO is approximately 10^{-3} atm or 1000 ppm. Since HCl concentrations in flue gases from the combustion of coal are far lower than 1000 ppm, no removal of hydrogen chloride by lime would be expected.

Consideration of the calculated equilibrium data for the reaction of HCl with other possible additives (MgO, BaO, NaOH, and KOH) indicates that of these materials, BaO and the alkali hydroxides are favorable for accepting HCl. Possibly, the addition of small amounts of one of these agents would remove HCl. Experimental data would be needed to verify the suitability of such materials and to determine the quantities of additives needed for HCl emission control. No work in this area is planned until other more pressing work is completed.

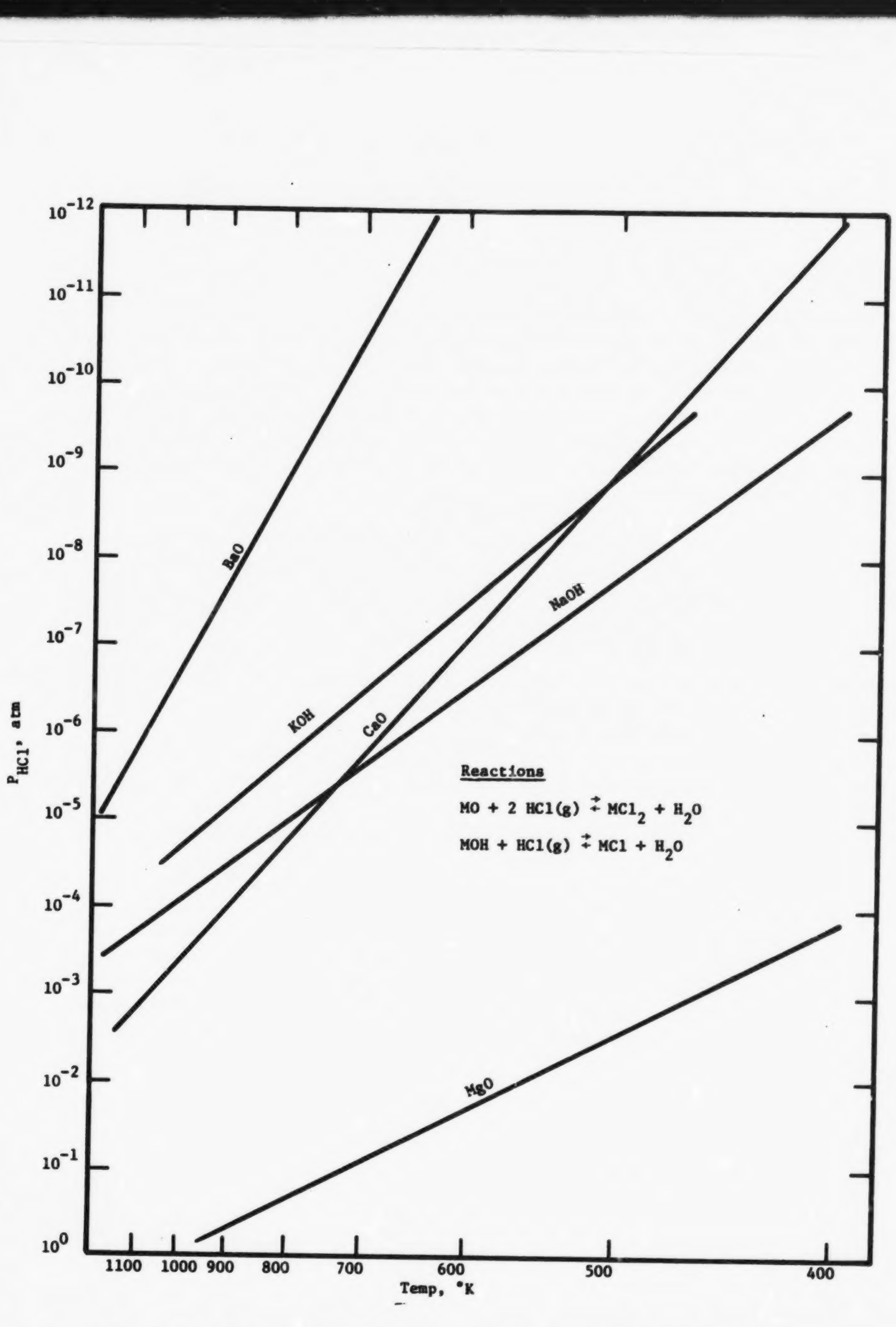

Fig. 25. Calculated Equilibrium Partial Pressure of HCl as a Function of Temperature ($P_{H_2O} = 0.1$ atm)

VII. FUTURE WORK

The future experimental program at ANL will encompass the following:

1. Completion of study of the effects of variables, such as coal particle size, for one-stage combustion at a pressure of 1 atm. Additional experiments at 1-atm pressure will be required to aid in establishing the mechanisms involved in pollution control. Studies having a lower priority include (a) measurement of SO_2 and NO levels during the combustion of oil in a fluidized bed under both oxidizing and reducing conditions and (b) experiments to determine pollutant removal with coals and limestones not yet tested.

2. Determination of the effect of independent variables on sulfur retention, NO level, and particulate emission, using the atmospheric-pressure bench-scale combustor in the two-stage mode of operation.

3. Construction of a multipurpose, bench-scale plant for operation at up to 10 atm to study the effects of the most important variables in

   a. one-stage, high-pressure combustion,
   b. two-stage, high-pressure combustion,
   c. regeneration of the partially sulfated and sulfided additives from one-stage and two-stage operation.

4. Continuation of studies to elucidate the mechanisms involved in one-stage and two-stage combustion and the regeneration reactions. In one-stage combustion, a sulfate is produced that is regenerated to oxide with a reducing gas; in two-stage combustion, a sulfide is produced that is regenerated by an oxidizing gas.

VIII. ACKNOWLEDGMENTS

We gratefully acknowledge the help given by Dr. R. C. Vogel, . D. S. Webster and Dr. S. Lawroski in directing and reviewing the gram, the assistance and advice of Mr. K. Natesan (Materials Science ision) in mounting the limestone particles and for performing some of e microprobe examinations, the assistance of Mr. A. Sanders and . A. Martin in mounting samples and of Mr. C. Johnson, Mr. K. Anderson, d Mr. C. Seils in performing microprobe examinations and of the analysis team of Mr. M. Homa, Mrs. C. Blogg, Miss F. Ferry, Miss J. Williams, and Mr. Z. Tomczuk directed by Dr. R. Larsen and Mr. E. Kucera, and of our typist Miss P. Wood.

APPENDIX A. MATERIALS

TABLE A.1. Size Distribution of Coals

Illinois. Seam 6, Peabody Coal Co.,
Mine 10, Christian County, Illinois

Welbeck. East Midlands Field (British National Coal Board)

	Sieve Analysis[a] (wt %)			
	As Charged to Hopper of Screw Feeder		After Feeding Through Screw Feeder	
U. S. Sieve No.	Illinois	Welbeck	Illinois	Welbeck
+14	-	-	N.A.[b]	-
-14 +25	19.4	11.3		14.0
-25 +35	13.5	13.9		15.4
-35 +45	16.9	23.1		21.0
-45 +80	18.9	27.8		22.0
-80 +170	13.2	9.9		11.1
-170 +325	7.6	7.0		7.4
-325	10.4	7.0		9.1
Average Particle Diameter, μm[c]	350	396		412

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[a] Analyses for Welbeck coal are for as-received material; the Illinois coal was ground to pass a U.S. No. 14 sieve before being fed.

[b] N.A. - not available.

[c] Calculated by summing products of weight fractions and average screen openings for the sieve size range.

TABLE A.2. Chemical Characteristics of Coals

Illinois. Seam 6, Mine 10, Peabody Coal Co.,
Christian County, Illinois

Welbeck. East Midlands Field (British National Coal Board)

Proximate Analysis[a] (wt %)

	As-Received		Dry Basis	
	Illinois	Welbeck	Illinois	Welbeck
Moisture	10.12	5.08	-	-
Volatile Matter	37.90	31.12	42.17	32.79
Fixed Carbon	41.12	46.65	45.75	49.15
Ash	10.85	17.16	12.08	18.07
Sulfur	3.7	1.23	4.14	1.30
Heating Value, Btu/lb	10956	11206	12163	11807

Ultimate Analysis[a] (wt %)

	Illinois	Welbeck
Carbon	68.45	67.05
Hydrogen	4.97	4.50
Sulfur	4.14	1.28
Nitrogen	1.18	1.21

Mineral Content of Ash[a] (wt %)

	Illinois	Welbeck
P_2O_5	0.12	0.19
SiO_2	38.67	58.65
Fe_2O_3	22.49	7.48
Al_2O_3	16.31	21.67
TiO_2	0.80	1.08
CaO	8.48	2.56
MgO	0.88	1.40
SO_3	8.59	2.13
K_2O	1.43	2.85
Na_2O	1.66	1.65
Undetermined	0.57	0.34

[a] Average of all analyses.

TABLE A.3. Size Distribution of Illinois Coal and Coarse Limestone No. 1359 Used in Experiment AR-6

U.S. Mesh	Illinois Coal (wt %)	Limestone Charged to Screw-Feeder Hopper (wt %)	Limestone after Passage through Screw Feeder (wt %)
+7		0	0
-7 +10		35.6	7.3
-10 +14		25.3	18.1
-14 +25	27.3	27.5	37.2
-25 +35	11.3	5.9	10.1
-35 +45	13.2	3.3	8.4
-45 +80	16.7	1.5	6.5
-80		0.9	12.5
-80 +170	14.6		
-170 +325	7.8		
-325	9.0		
Av. particle dia, μm	490	1637	1010

TABLE A.4. Chemical Characteristics and Particle Size Distribution for Pittsburgh Coal

Mineral Content of Ash (wt %)		Sieve Analysis		
		U.S. Mesh	As Received (wt %)	As Used in Current Runs (wt %)
P_2O_5	0.26	+4	33.4	0
SiO_2	48.51	-4 +14	41.0	0
Fe_2O_3	15.17	-14 +25	16.0	22.0
Al_2O_3	22.54	-25 +45	5.8	30.0
TiO_2	1.01	-45 +80	1.4	21.1
CaO	3.93	-80 +170	0.9	13.1
MgO	0.80	-170 +200	1.5	4.0
SO_3	4.54	-200		9.8
K_2O	1.73			
Na_2O	0.66			
Undetermined	0.86			

[a] As received.

TABLE A.5. Chemical Composition of Limestones

Limestone No. 1359, M. J. Grove Lime Co., Stephens City, Va.

British Limestone, J. Gregory & Son, Stoke-on-Kent, Staffordshire

Chemical Analysis[a] (wt %)

Component	Limestone No. 1359	British Limestone ANL Analysis	British Limestone CRE Analysis
Ca	37.9	37.9	39.1
Mg	0.27	0.12	0.12
CO_2	NA[b]	49	42
H_2O	1.56	0.8	NA
SiO_2	NA	NA	1.6
Derived			
$CaCO_3$	94.80	94.6	96.5
$MgCO_3$	0.95	0.4	0.4

[a] For as-received material.

[b] NA - not available.

TABLE A.6. Size Distribution of Limestones

Limestone No. 1359, M. J. Grove Co., Stephens City, Va.

British Limestone, J. Gregory & Son, Stoke-on-Kent, Staffordshire

U.S. Sieve No.	Sieve Analysis (wt %)			
	As Charged to Hopper of Screw Feeder		After Feeding Through Screw Feeder	
	1359	British[a]	1359	British
+12	-	-	-	-
-12 +14	-	2.7	-	-
-14 +25	39.3	29.8	33.1	22.6
-25 +35	14.0	13.7	14.2	12.8
-35 +45	13.8	13.7	14.6	13.6
-45 +80	12.5	13.3	13.8	14.2
-80 +170	7.9	9.7	9.0	11.6
-170 +325	3.5	5.7	4.2	9.0
-325	9.0	11.3	11.1	16.1
Average Particle Dia,[b] μm	609	555	555	440

[a] For as-received material.

[b] Calculated by the procedure described in footnote c, Table A.1.

TABLE A.7. Characteristics of Welbeck Coal Ash

Constituent	Mineral Analysis, Ignited Basis (wt %)	U.S. Mesh	Sieve Analysis (As Received) (wt %)
P_2O_5	0.06	+25	24.5
SiO_2	69.74	-25 +35	20.2
Fe_2O_3	4.76	-35 +45	30.6
Al_2O_3	20.34	-45 +80	22.1
TiO_2	0.81	-80 +170	1.5
CaO	3.70	-170 +325	0.5
MgO	2.05	-325	0.5
SO_3	2.44		
K_2O	2.98		
Na_2O	1.73		
Undetermined	0.39		

APPENDIX B. AUXILIARY EQUIPMENT AND INSTRUMENTATION

1. Heating-Cooling System

Two 2.7-kW, 230-V resistance heaters are the external source of heat for the lower portion of the 4-ft combustion section and a 2.0-kW, 230-V heater for the bubble-cap section. These heaters assist in bringing the fluid bed to the coal ignition temperature of ~800°F and in maintaining the heat balance in the reaction system. The locations of the heating circuits and of the controlling and recording thermocouples on and in the combustor are shown in Fig. B.1. Stainless steel-sheathed Chromel-Alumel thermocouples are used. The temperature indicator-controllers are Honeywell-Brown Pyro Vanes with indicating-controlling ranges of either 0-2000°F or 0-2400°F. Thermocouple output is displayed on a Honeywell-Brown Electronik 12-point, 0-2400°F range recorder.

Removal of heat from the combustor is accomplished by passing air or an air-water mist through the annular chambers surrounding the lower portion of the combustor section. When it is necessary to remove only relatively small quantities of heat, air alone is circulated. The flow of air (metered with a rotameter) is adjusted to obtain the desired output of a thermocouple immersed in the fluid bed. When a greater quantity of heat must be removed, air-water mist is injected into the annular chambers. A schematic of one of four systems for the injection of air-water mist is shown in Fig. B.2. The other three systems are similar. The system consists of a 5-gal distilled water reservoir, an air supply, and a temperature indicator-controller (TIC) - thermocouple - solenoid valve combination. The thermocouple immersed in the fluidized bed acts through the TIC to energize a solenoid valve which, in turn, allows water to be injected into a carrier air flow and hence to the annular chamber of the combustor. The air-water mist leaving the combustor is vented through a heat-exchanger to remove the water.

2. Solids Injection and Removal

Coal and limestone are transported to the fluidized-bed reactor as a dilute phase in an air stream that is part of the total fluidizing-air flow. The solids are delivered into the air stream by Vibra Screw Line bin feeders. The standard units have solids bins of 3-cu ft capacity, solids contact surfaces of Type 304 stainless steel, and mechanical variable-speed transmissions with a 10 to 1 turndown ratio. They can utilize screws of various diameters (in the range 1/4 to 5/8 in.), depending on the feed rate requirements. Solids feed rates of 0.2 to 17 lb/hr are employed. To maintain a continuous check of the weight of the contents of Vibra Screw feeders, the feeders are mounted on Toledo "One Spot" platform scales, each with a capacity of 500 lb; the smallest scale division on these scales is 1/2 lb.

The dilute-phase air-solids mixture is carried to the combustor in 3/8-in. stainless steel lines. Coal and limestone are injected separately into the combustor through a fitting welded to the combustor at a point just above the gas distributor plate.

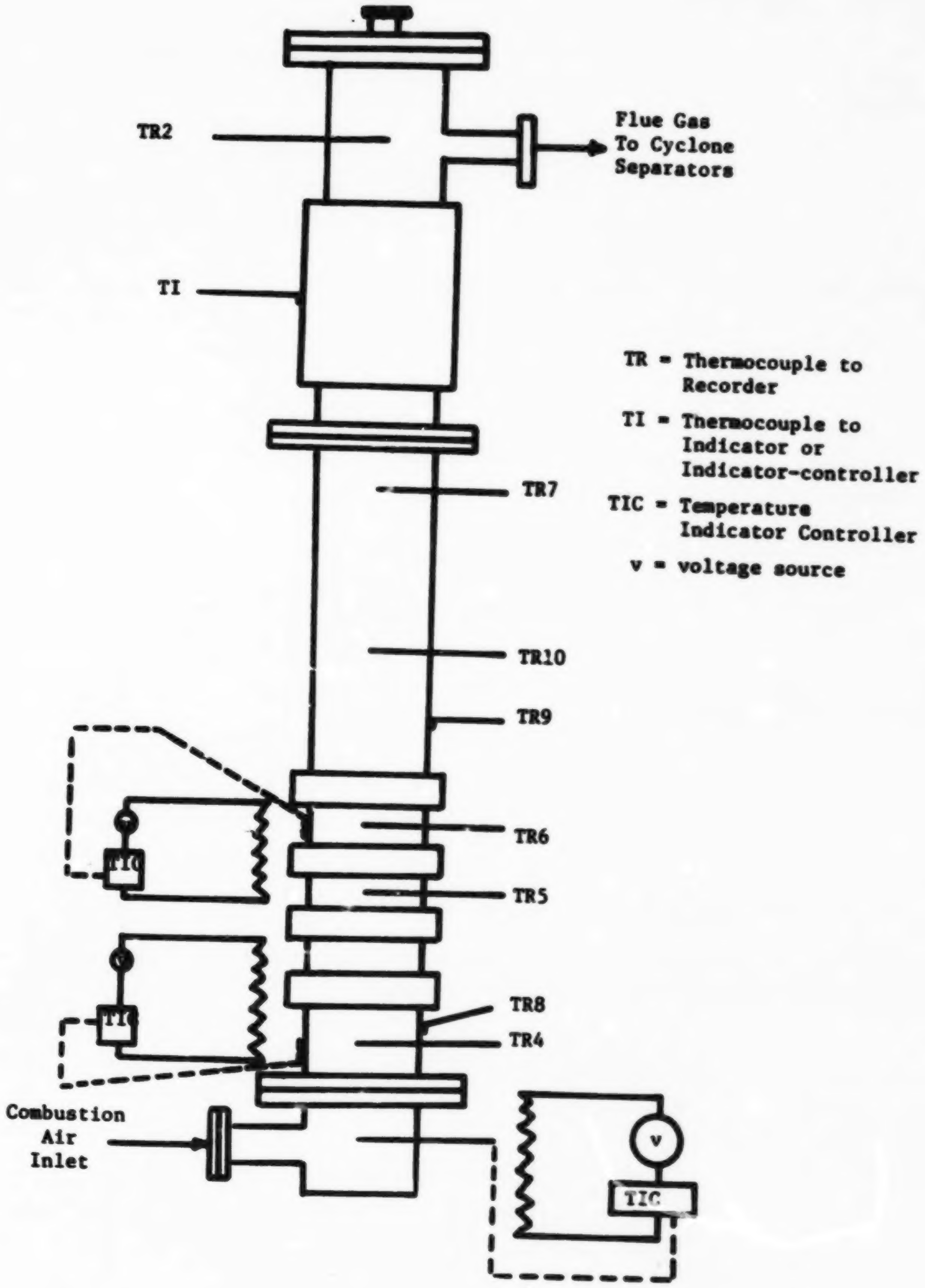
TR2
Flue Gas
To Cyclone
Separators
TI
TR = Thermocouple to Recorder
TI = Thermocouple to Indicator or Indicator-controller
TIC = Temperature Indicator Controller
v = voltage source
TR7
TR10
TR9
TR6
TIC
TR5
TIC
TR8
TR4
Combustion
Air
Inlet
v
TIC

Fig. B.1. Heating and Temperature Sensing Arrangements for Combustor

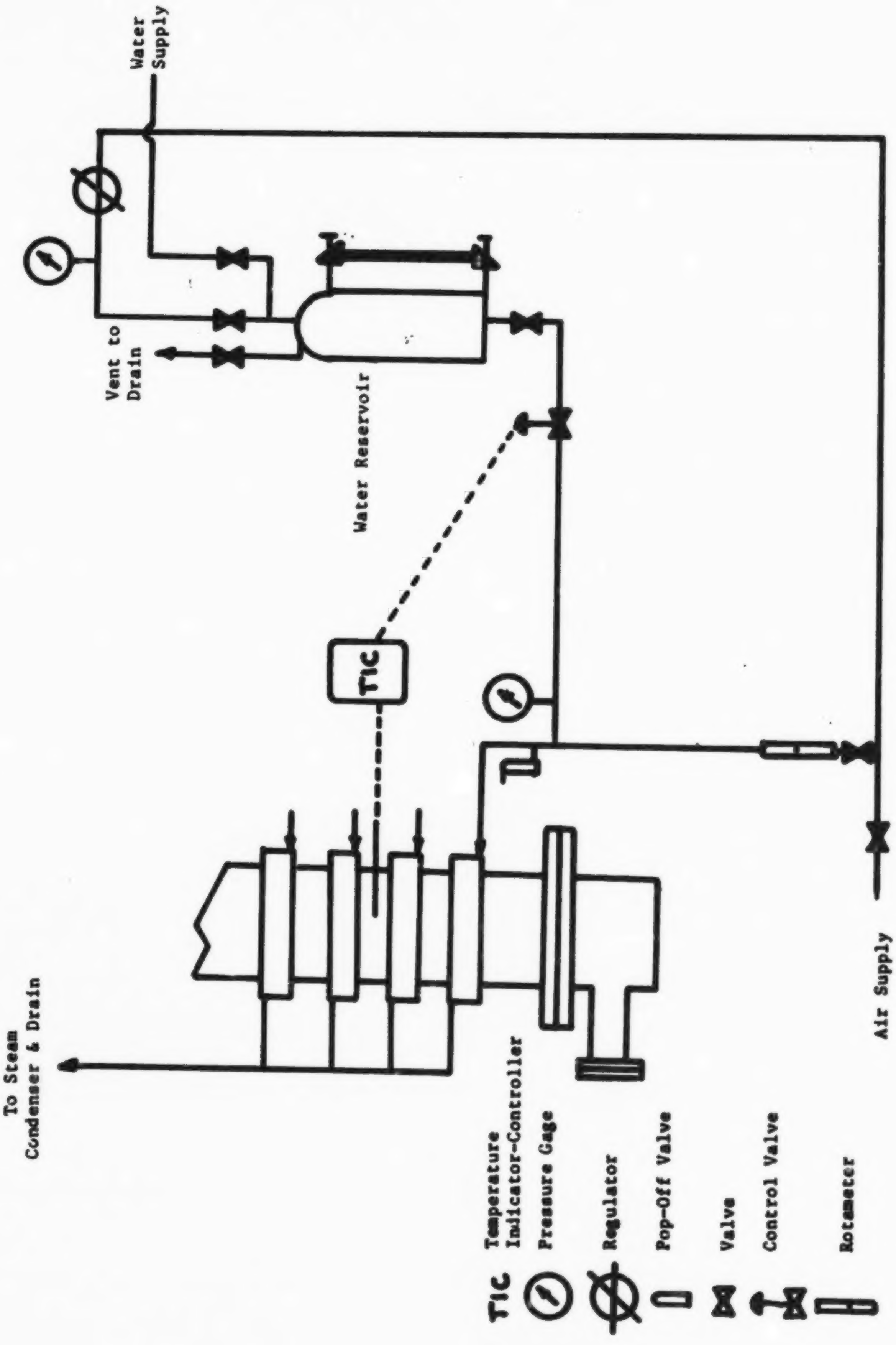
Water Supply
Vent to Drain
Water Reservoir
TIC
To Steam Condenser & Drain
Air Supply
TIC Temperature Indicator-Controller
Pressure Gage
Regulator
Pop-Off Valve
Valve
Control Valve
Rotameter

Fig. B.2. Combustor Cooling Circuit

Solids leave the combustor (1) as bed samples, (2) as excess bed material, and (3) as flyash-limestone fines. Samples are removed from the combustor bed through 1/2-in. stainless steel pipes welded into the combustor wall at points about 2 and 20 in. above the gas distributor plate. The solids sampling system consists of a manifold that provides access to a vacuum pump, high-pressure (35-psig) air, and the sampling ports on the combustor. Solids are drawn into an evacuated sampling vessel by opening a valve connecting the vessel to a combustor port for a sufficient time to withdraw ~50-100 g of the bed material. The sample is then allowed to cool, the sampling vessel is brought to atmospheric pressure, and a bottom valve on the sampling vessel is opened to allow the bed sample to flow out. Details on procedures for elemental analysis and coal analysis are presented in Table B.1.

TABLE B.1. Analytical Methods and Procedures

A. Methods for Elemental Analysis

1) Calcium. EDTA volumetric titration.

2) Sulfur. Leco combustion method, employing automatic volumetric titration of an $IO_3^{=}$ -I-starch system.

3) Carbon. Leco combustion method, using a thermal-conductivity detector and employing the O_2/CO_2 relationship.

4) Carbonate. Measurement, with a sensitive gas chromatograph, of the CO_2 evolved by acidifying the material.

5) Sulfite, $SO_3^{=}$. Turbidimetric method. The sulfur value released by acid treatment is converted to sulfate and titrated with a barium solution.

6) Sulfide, $S^{=}$. Turbidimetric method. A sample is treated with HCl; the evolved gases are collected in an inert atmosphere and then treated with an acidic acid-bismuth nitrate solution. Bismuth sulfide precipitates and is measured.

7) Combined Nitrogen. Micro-Kjeldahl method. The nitrogen is released as ammonia, absorbed, and titrated.

B. Methods for Analysis of Coal and Coal Ash

Analyses of coal and coal ash are performed by a commercial laboratory (Commercial Testing and Engineering Co., South Holland, Ill.) employing ASTM designation D271-64 methods. The analyses made are as follows: proximate, ultimate, mineral (ash), fusibility of ash, free swelling index, and calorific value.

Bed material is removed intermittently during a run to maintain a constant bed height; after a run, the entire bed is removed. Bed material is withdrawn through a 1-in. pipe. The top of the pipe is at the face of the gas distributor, and the pipe passes through the plenum chamber and its bottom plate. When a plug valve at the bottom of the pipe is opened, bed material flows out of the reactor.

Most of the fine flyash and limestone carried in the flue gas stream are removed by two cyclone separators in series. Essentially all of the remaining fines are removed with a glass wool final filter.

3. Air Preheater

The preheater is constructed of a 7-ft length of 3-in. dia schedule 40, type 304 stainless steel pipe. Figure B.3 is a schematic of the unit. The preheater is packed with 6.5-ft lengths of 3/8-in. dia type 304 stainless steel tubing to increase the heat exchange capacity.

Heating is provided by four Hevi-Duty clam-shell furnaces which cover the entire length of the preheater. The top furnace is rated at 1.6 kW and the other three are each rated at 3.4 kW; all are operated at a 230-V input. Temperature control is accomplished with thermocouple, temperature-indicator-controller (TIC) circuits as shown in Fig. B.3. These units are identical to those used for the combustor.

4. Fluidizing-Combustion Air Supply

Fluidizing-combustion air is taken from the laboratory high-pressure (49 psig) air supply. After passing through a pressure reducer where the pressure is reduced to 15 psig, the filtered air is metered through a flow control system to the preheater. Figure B.4 is a diagram of the flow control system. This system consists of a Taylor pressure transmitter, a flow recording and control device, and two calibrated orifice-flow control valve arrangements. The ranges of the two orifice-valve combinations are 0-15 and 0-32 scfm.

An example of air flow rates in a run is as follows: To achieve superficial gas velocity of 3 ft/sec in the combustor at 1472°F, a total flow rate of 10 scfm at 70°F and 1 atm is needed. This total flow is divided as follows: 6.5 scfm through the orifice-valve arrangement to the preheater, 1.5 scfm through each of the solids feeders, and 0.5 scfm through an auxiliary feed port.

5. Flue Gas Filtration

The approximately 10 scfm (70°F, 1 atm) of flue gas leaving the combustor is passed through a particle-removal system before it is routed through the building exhaust system. The particle-removal equipment comprises two cyclone separators and a glass wool final filter.

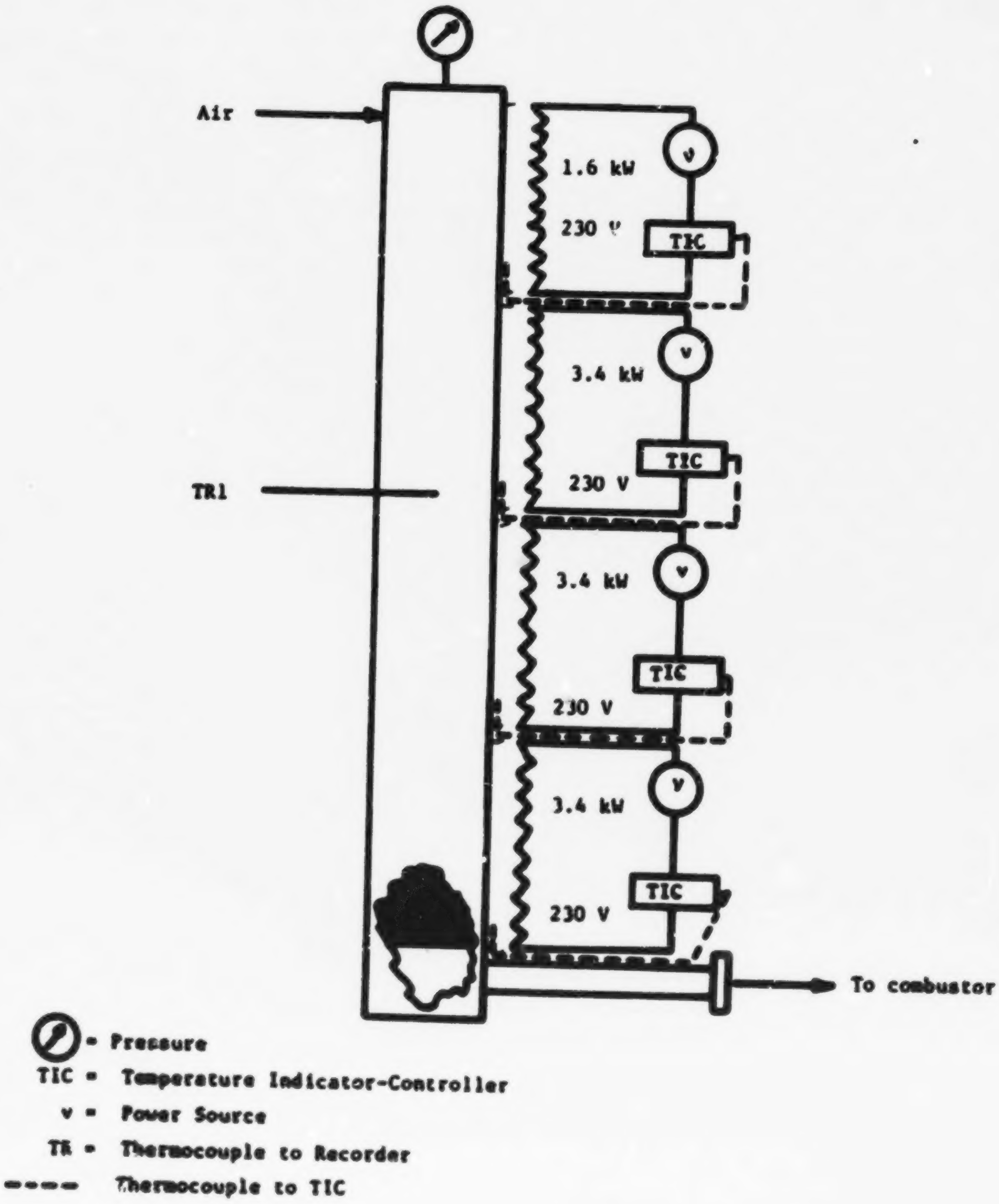
Air
1.6 kW
230 V
TIC
3.4 kW
TIC
230 V
TR1
3.4 kW
TIC
230 V
3.4 kW
TIC
230 V
To combustor
= Pressure
TIC = Temperature Indicator-Controller
v = Power Source
TR = Thermocouple to Recorder
Thermocouple to TIC

Fig. B.3. Preheater

The cyclones were manufactured by Universal Oil Products (UOP) Air Correction Division and are designated sizes 2 and 3 (see UOP Tech. Bull. 604A). The calculated flow handling capacities for a gas at 500°F and a ΔP of 6-in. water gauge are 49 and 111 cfm for size 2 and size 3 cyclones, respectively.

The final process filter is a 2-sq ft, 1-in.-thick glass fiber commercial unit that constitutes one side of a filter box. The flue gas is passed through this filter and into the room exhaust system. In the latter system, the gas (after a manyfold dilution) passes through a set of high-efficiency filters before it is exhausted to the atmosphere.

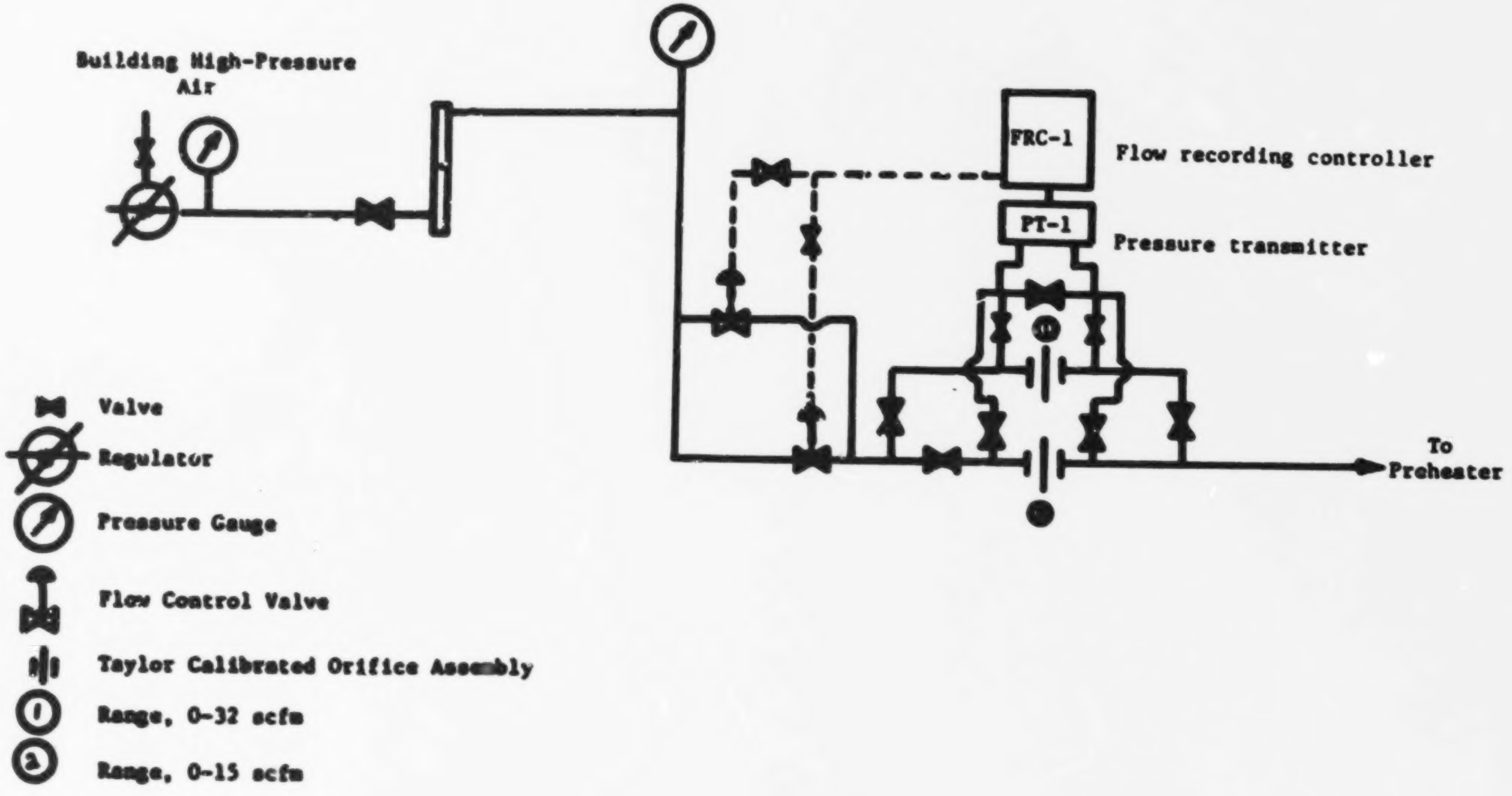
Building High-Pressure Air
FRC-1
Flow recording controller
PT-1
Pressure transmitter
To Preheater
Valve
Regulator
Pressure Gauge
Flow Control Valve
Taylor Calibrated Orifice Assembly
Range, 0-32 scfm
Range, 0-15 scfm

Fig. B.4. Fluidizing-Combustion Air Flow Control System

6. Gas Sampling and Analysis System

A sample of approximately one-twentieth of the total flue gas (0.5 scfm) is taken at a point midway between the primary and secondary cyclones. This stream is pumped through a 12-in. sintered-nickel bayonet filter to remove solids. The gas is then passed through a water condenser and a refrigerator to remove water. Any residual water, which could interfere with the measurement of flue-gas constituents by an infrared technique, is removed by magnesium perchlorate. (About 3000 ppm moisture in the gas gives a reading corresponding to ∿30 ppm SO_2 and ∿20 ppm NO. Moisture does not affect oxygen analysis.)

Continuous analyses for NO and SO_2 are carried out using Beckman 315A infrared analyzers, and continuous analyses for CH_4 and CO with Mine Safety Appliance (MSA) MRA infrared analyzers. Continuous measurement of oxygen is accomplished with a Hays paramagnetic oxygen analyzer. Intermittent analyses for CO_2 are performed by gas chromatography. The instrument supply manifold is maintained at a constant pressure by a pressure-control device. Aliquot samples are removed from the manifold to supply each instrument with the required gas flow. Prior to and during an experiment, the response of each analyzer to nitrogen gas and to a mixture of the analyzed component in nitrogen are determined and the instrument zero and span are adjusted, if necessary. The analytical equipment components are listed in Table B.2. The temperature of the gas is determined at several parts of the sampling system, and values of the gas-residence time are calculated. It was estimated that the total residence time of flue gas in the sampling system is about 12 sec.

7. Data Logger

The combustor pilot plant has recently been equipped with a Honeywell data logger capable of handling up to 200 variables: 175 thermocouple signals, 19 pneumatic signals, and 6 millivolt signals. During a log cycle, a record of the 200 variables (in groups of 25) with time and calibration data (system check) is recorded by a Flexowriter typewriter. Simultaneously, the same information is stored on punched tape. Information ultimately is stored on data cells for use in the IBM 360-50/75 computer and Calcomp plotter systems.

The heart of the logger is the digitizing servo, which is connected sequentially to each of the 200 channels to receive the input voltage, measure it, and establish an analog shaft rotation position. This shaft position is encoded in cyclic binary form by a Giannini encoder for later translation into the decimal form used by the typewriter.

TABLE B.2. Flue Gas Analytical Equipment

Flue Gas Constituent	Method of Analysis	Instrument Model	Output Displayed On	Range	Accuracy (% of range)
Sulfur Dioxide	Infrared	Beckman 315A	Bristol, two-pen, variable-range recorder	0-5000 ppm 0-10,000 ppm	±1%
Nitric Oxide	Infrared	Beckman 315A	Bristol, two-pen, variable-range recorder	0-500 0-1000 ppm	±1%
Oxygen	Paramagnetism	Hays 632	Honeywell-Electronik 16, 2-pen, 0-10 mV range recorder	0-1 vol % 0-10 vol %	
Methane	Infrared	MSA LIRA 200	Honeywell-Electronik 16, 2-pen, 0-10 mV range recorder	0-1000 ppm	±1%
Carbon Monoxide	Infrared	MSA LIRA 300	Honeywell-Brown Electronik variable range	0-5000 ppm	±1%
Carbon Dioxide	Gas Chromatography	Hewlett Packard 700	Honeywell-Electronik 16, variable chart speed, reversed-drive recorder	0-20 vol %	±5%

APPENDIX C. MATERIAL BALANCES

Material balances were calculated from the sulfur, carbon, and calcium contents of (1) the input streams (coal, limestone additive, and initial fluid bed) and (2) the output streams (cyclone solids, final bed, bed samples, and SO_2, CO_2, CO, and CH_4 contents of the flue gas).

The weights of material in the solids input streams (coal and limestone additive) were obtained from feed hopper scale readings taken during the runs. The accuracy of these weights was checked by direct weighing of the quantities of coal and limestone charged to the solids feeders and of the quantities remaining in the solids feeders at the end of an experiment. The quantities of sulfur, carbon, and calcium in these input streams were calculated from available analytical data. For the solids output streams (material on the cyclones, bed samples, and final bed), the quantity accumulated or removed was weighed, then sampled and analyzed for sulfur, carbon, and calcium.

The quantities of sulfur and carbon in the flue gas were estimated from data supplied by continuous monitoring for SO_2, CO, and CH_4 by IR analyzers and from periodic analyses for CO_2 by gas chromatography. The flue gas composition data were integrated to determine the total quantity of either sulfur or carbon exhausted in the flue gas over the full course of an experiment.

Material balances for sulfur, carbon, and calcium in Amer-1, -3, and -4 are given in Table C.1 and those for Brit-1 to -3, Brit-Amer, and Amer-Brit in Table C.2. The results of the material balance calculations for the five final BC-series experiments are listed in Table C.3 and those for the AR-series experiments in Table C.4.

TABLE C.1. Material Balance for Sulfur, Carbon, and Calcium, Experiments Amer-1, -3, and -4 (weights in pounds)

	Amer-1				Amer-3				Amer-4			
	Weight[a]	S	C	Ca	Weight[a]	S	C	Ca	Weight[a]	S	C	Ca
Material In												
Coal	326.0	12.13	200.56	2.15	108.5	4.04	72.17	0.72	71.2	2.65	43.81	0.47
Additive	59.1	-	6.74	22.40	34.5	-	3.93	13.08	13.7	-	1.56	5.19
Bed	16.9	1.79	0.17	6.52	16.1	1.80	0.16	5.59	14.3	1.53	0.14	5.62
Σ	-	13.92	207.5	31.1	-	5.84	76.3	19.4	-	4.2	45.5	11.3
Material Out												
Flue Gas	-	6.36	195.45	-	-	1.23	63.96	-	-	1.09	40.28	-
Primary Cyclone	58.9[b]	2.78	12.30	7.68	16.8	0.55	2.74	3.40	9.83	0.24	2.41	1.26
Secondary Cyclone	-	0.07	0.88	0.26	2.9	0.07	0.64	0.44	1.09	0.02	0.29	0.15
Final Filter	c	-	-	-	c	-	-	-	1.46	-	-	-
Fluidized Bed	52.3	7.80	0.31	17.74	37.0	4.54	0.36	18.13	21.7	2.35	0.21	7.65
Σ	-	17.01	208.94	25.68	-	6.39	67.70	21.97	-	3.7	43.2	9.1
% Balance	-	122	101	83	-	109	89	113		88	95	82
All experiments, balance = $\frac{\text{Total in} \times 100}{\text{Total out}}$										113	97	92

[a] Weight, for example, of coal fed in specified run(s).

[b] This is the total weight of the material removed from the primary and secondary cyclones in this run.

[c] Not available.

TABLE C.2. Material Balance for Sulfur, Carbon, and Calcium, Experiments Brit-1 to -3, Brit-Amer, and Amer-Brit (weights in pounds)

	Brit-1				Brit-2				Brit-3				Brit-Amer				Amer-Brit			
	Weight[a]	S	C	Ca	Weight[a]	S	C	Ca	Weight[a]	S	C	Ca	Weight[a]	S	C	Ca	Weight[a]	S	C	Ca
Material In																				
Coal	141.3	1.74	65.89	0.44	60.0	0.74	27.99	0.19	96.6	1.19	45.06	0.30	30.9	0.38	14.41	0.10	54.7	2.05	33.96	0.36
Additive	10.9	-	1.34	4.20	10.2	-	1.25	3.93	4.6	-	0.57	1.77	1.5	-	0.17	0.56	11.6	-	1.43	4.49
Bed	19.0	0.18	-	0.44	16.1	0.47	0.16	1.50	-	-	-	-	-	-	-	-	-	-	-	-
Σ	-	1.92	67.23	5.08	-	1.21	29.40	5.62	-	1.19	45.63	2.07	-	0.38	14.58	0.66		2.05	35.39	4.85
																	Σ[b]	4.83	125.00	13.20
Material Out																				
Flue Gas	-	0.69	75.73	-	-	0.15	31.77	-	-	0.56	51.46	-	-	c	-	-	-	0.65	30.32	-
Primary Cyclone	29.3	0.15	10.00	1.61	12.9	0.09	4.01	1.10	18.2	0.13	8.54	0.86	7.4	-	-	-	10.2	0.31	1.74	2.05
Secondary Cyclone	2.6	0.02	1.28	0.11	1.1	0.01	0.46	0.07	1.6	0.02	1.08	0.07	0.7	-	-	-	1.1	0.02	0.22	0.13
Final Filter	4.5	0.18	0.62	0.20	2.1	0.02	0.24	0.07	1.7	0.02	0.53	0.07	d	-	-	-	0.5	0.02	0.07	0.04
Fluidized Bed[e]	34.4	1.02	0.43	2.28	7.4	0.29	0.08	1.25	11.4	0.59	0.13	2.40	2.6	-	-	-	21.5	1.66	0.20	4.54
Σ		2.06	88.06	4.20	-	0.56	36.56	2.49	-	1.32	61.74	3.40	-	-	-		-	2.66	32.55	6.76
																	Σ[b]	4.54	130.85	12.65
% Balance		107	131	83														94	105	96
All Experiments, Balance																		98	114	92

[a] Weight, for example, of coal fed in a specified run.

[b] Summation of Brit-2, -3, Brit-Amer, and Amer-Brit. Material balance is for total.

[c] Included in Brit-3.

[d] Combined with Brit-3.

[e] Includes the fluid bed in experiments Brit-1 and Amer-Brit; includes only the fluid-bed samples and the excess bed in other experiments.

TABLE C.3. Material Balance for Sulfur, Carbon, Calcium, and Magnesium, Experiments BC-6 to -10 (weights in pounds)

	BC-6			BC-7			BC-8			BC-9			BC-10			
	S	C	Ca	S	C	Ca	S	C	Ca	S	C	Ca	S	C	Ca	Mg
Material In																
Coal	4.23	60.47	0.47	5.30	74.70	0.58	6.41	90.29	0.70	5.59	78.83	0.61	5.70	80.37	0.62	-
Additive[a]	-	0.67	2.23	-	4.08	13.40	-	4.54	14.89	-	4.45	11.10	-	9.20	15.08	9.41
Bed[b]	1.50[c]	-	11.43	3.42	1.65	8.43	2.02	1.14	7.02	1.47	0.79	7.33	1.99	1.39	6.40	-
Σ	5.7	61.1	14.1	8.7	80.4	22.4	8.4	95.9	22.6	7.1	84.1	19.0	7.7	91.0	22.1	9.4
Material Out																
Flue Gas	0.81[d]	56.21[e]	-	0.99[d]	64.04[e]	-	0.96[d]	82.97[e]	-	1.63[d]	76.67[e]	-	0.78[d]	74.89[e]	-	-
Primary Cyclone	0.42	3.29	1.64	0.87	7.04	2.81	0.49	6.31	1.63	0.94	4.24	6.61	2.22	4.94	13.35	7.57
Secondary Cyclone	0.05	0.45	0.21	0.44	5.88	0.22	0.02	6.37	0.12	0.09	0.61	0.65	0.04	0.25	0.03	0.09
Final Filter	0.09	0.12	0.11	0.06	0.13	0.09	0.03	0.08	0.07	0.11	0.16	0.17	0.11	0.17	0.14	0.08
Fluidized Bed Samples	3.83	1.73	9.45	4.73	2.77	15.79	4.08	2.42	17.56	3.43	2.36	9.47	3.30	0.38	7.16	1.55
Σ	5.2	61.8	11.4	7.1	79.9	18.9	5.6	92.2	19.4	6.2	84.0	16.9	6.4	80.6	20.7	9.3
% Balance	91	101	81	81	99	84	66	96	86	88	100	89	84	89	94	99
All Experiments, Balance														83	97	87

[a] Limestone No. 1359 (97.8% $CaCO_3$, 1.3% $MgCO_3$) used in experiments BC-6, -7, and -8; Limestone No. 1360 (69.8% $CaCO_3$, 19.2% $MgCO_3$) used in BC-9; Dolomite No. 1337 (53.4% $CaCO_3$, 46.5% $MgCO_3$) used in BC-10.

[b] New starter bed of limestone No. 1359 was sulfated in experiment BC-6. This bed or part of it was then carried over in each following experiment.

[c] This quantity of sulfur was added as SO_2 from a gas cylinder during initial bed sulfation.

[d] Calculated from time-averaged concentration of SO_2 in the flue gas.

[e] Calculated from time-averaged concentrations of CO_2, CO, and CH_4 in the flue gas.

TABLE C.4. Material Balances for Sulfur, Carbon, and Calcium, Experiments AR-1, -2, -4, -5, and -6 (weights in pounds)

	AR-1			AR-2			AR-4			AR-5			AR-6		
	S	C	Ca	S	C	Ca	S	C	Ca	S	C	Ca	S	C	Ca
Material In															
Coal	5.48	77.28	0.60	5.61	79.02	0.61	8.67	126.85	1.36	11.06	182.96	1.96	16.67	275.60	2.95
Additive	-	5.12	16.81	-	5.59	18.38	-	4.86	15.95	-	17.68	58.10	-	27.66	90.87
Bed	2.27	0.06	4.66	1.78	1.03	6.32	-	3.14	10.32	1.57	0.19	7.54	1.73	0.36	16.57
Σ	7.8	82.5	22.1	7.4	85.3	24.9	8.7	134.9	27.6	12.6	200.8	67.6	18.4	303.6	110.4
Material Out															
Flue Gas	1.72	65.58	-	0.42	76.62	-	1.04	119.64	-	0.63	198.02	-	2.09	262.29	-
Primary Cyclone	1.73	5.75	7.57	0.64	3.99	3.70	0.67	8.36	4.65	0.58	3.99	3.58	3.44	29.12	27.67
Secondary Cyclone	0.04	0.53	0.16	0.03	0.56	0.15	0.04	0.83	0.25	0.04	0.60	0.20	0.20	1.17	0.93
Final Filter	0.09	0.18	0.14	0.09	0.23	0.21	0.11	0.71	0.18	0.02	0.24	0.12	0.08	0.33	0.22
Fluidized Bed and Samples	3.84	1.96	14.10	4.99	1.64	16.40	4.84	0.48	17.09	8.76	1.05	42.17	9.03	1.64	67.23
Σ	7.4	74.0	22.0	6.2	83.6	20.5	6.7	129.5	22.2	10.0	203.9	46.1	14.8	294.5	96.1
% Balance	96	90	100	83	97	82	77	96	80	79	102	68	81	97	87
All Experiments, Balance													82	97	82

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